THE TEMPERATURE DEPENDENCE OF EXCESS THERMODYNAMIC PROPERTIES OF N-HEPTANE-TOLUENE AND METHYLCYCLOHEXANE-TOLUENE SYSTEMS

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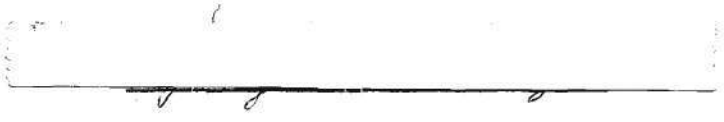

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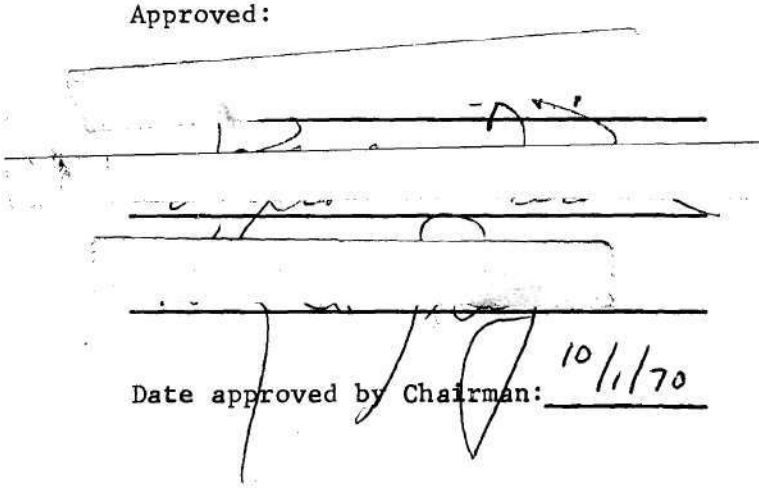

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LIST OF SYMBOLS

The symbols used in the text, unless otherwise stated, have the following meaning:

A	coefficient in Redlich-Kister equation
a	coefficient in Redlich-Kister equation
C	heat capacity; coefficient in Redlich-Kister equation
d	parameter of non-central forces
E	any extensive thermodynamic property
e	parameter of central forces
G	Gibbs free energy
g	angular function
H	enthalpy
I	a constant
k	Boltzmann constant
M	molecular weight
m	mass; number of constants used in fit
n	mole number; number of data points
P	pressure
R	gas constant
S	entropy
s	volume parameter
T	temperature (in Kelvins)
t	temperature (in centigrades)
U	energy

u	intermolecular potential
V	volume
X	interaction parameter
x	mole fraction
y	sum of squares of residuals
z	standard deviation

Greek Alphabet

α	coefficient of thermal expansion
β	isothermal compressibility
γ	activity coefficient
Δ	parameter of non-central forces
δ	parameter of non-central forces
ϵ	energy parameter
ρ	density
Σ	summation
σ	length parameter
ω	angular coordinate

Subscripts

c	of can
f	of fusion
i,j	referring to components in mixture
m	mean; of melting point
p	at constant pressure
s	of sample
T	at constant temperature
v	at constant volume; of vaporization

x	at constant composition
o	of reference species; of integration constant
1,2	initial and final; referring to components in mixture

Superscripts

E	excess property
M	property of mixing
~	molar quantity
*	statistical average

SUMMARY

The objective of this research was to determine excess thermodynamic properties of the systems n-heptane-toluene and methylcyclohexane-toluene over a wide temperature range and to examine these results using molecular solution theories.

Heat capacities of the pure components and several mixtures were measured in a precision adiabatic calorimeter. Melting point studies showed that the purity of all materials exceeded 99.7 mole per cent. The melting points of the pure substances agreed with good literature values within 0.02 K.

Heat capacities of five mixtures of n-heptane and toluene were measured from 182 to 312 K, at compositions of 0.18810; 0.34751; 0.50341; 0.66119; and 0.82359 mole fraction n-heptane. Heat capacities of five mixtures of methylcyclohexane and toluene were measured from 162 to 312 K, at compositions of 0.16728; 0.31372; 0.53541; 0.66700; and 0.82676 mole fraction methylcyclohexane. For comparison, the heat capacity of one mixture of n-heptane and methylcyclohexane (composition: 0.48910 mole fraction n-heptane) was measured from 182 to 312 K. The heat capacities are believed accurate within 0.2 per cent. They generally agree well with good literature data.

Densities of the pure components and their mixtures (at the compositions listed above) were measured at 293.15 K in a Bingham pycnometer, with an accuracy of 0.00003 g/cm^3.

Excess heat capacities were computed from the heat capacities

of the pure components and their mixtures. Using these results and excess enthalpy and free energy data near room temperature reported in the literature, excess enthalpies, free energies, entropies, and activity coefficients were computed as functions of temperature and composition using the Redlich-Kister representation. The excess enthalpy, free energy, and entropy for the mixture of n-heptane and methylcyclohexane were derived as functions of temperature.

Excess volumes at 293.15 K were derived from the density measurements.

The excess thermodynamic functions of both title systems show a nearly quadratic dependence on composition. The excess enthalpy, free energy, and entropy are positive and increase with decreasing temperature. Both systems show very similar behavior except below 220 K, where the temperature dependence of the excess enthalpy and entropy is larger for n-heptane-toluene than for methylcyclohexane-toluene. The system n-heptane-methylcyclohexane is nearly ideal at room temperature, but the excess enthalpy and entropy reach large values at low temperatures. The maximum of the excess volume at 293.15 K is 0.15 cm^3/mole for n-heptane-toluene, 0.39 cm^3/mole for methylcyclohexane-toluene and -0.01 cm^3/mole for n-heptane-methylcyclohexane.

The results were interpreted using the conformal solution theory[24], a theory of Rowlinson and Sutton[37] assuming orientation-dependent intermolecular forces, and a theory of Flory[15] for mixtures of nonspherical molecules. Only the theory of Rowlinson and Sutton was able to predict the observed temperature dependence of the excess enthalpy, free energy, and entropy. This suggests that directional intermolecular

forces (possibly caused by π-electron interactions between toluene molecules) influence the behavior of these systems. However, the theory of Flory succeeded best in explaining the observed excess volumes.

CHAPTER I

INTRODUCTION

Although many workers have studied the properties of liquid mixtures and many theories have been proposed to correlate the results, no comprehensive theory of liquid mixtures has been presented so far. Liquids and liquid mixtures are characterized by the presence of strong intermolecular forces. Even when the nature of these forces is known, mathematical difficulties prohibit an exact derivation of the thermodynamic functions using the laws of statistical mechanics. Approximate methods have therefore been developed which are tailored to specific types of systems. Many of these methods have been described in monographs by Rowlinson[35,36] and Prigogine[30].

The nonideality of a liquid mixture is usually described by excess thermodynamic functions, like the excess Gibbs free energy, G^E, the excess enthalpy, H^E, the excess energy, U^E, the excess entropy, S^E, the excess heat capacity, C_p^E, and the excess volume, V^E. Most of the reports in the literature give these excess properties as a function of mixture composition, but usually only at one temperature or over a narrow range of temperatures. Clearly, more information could be obtained by studying the dependence of these properties on both composition and temperature for selected systems. This is the main object of this work.

The systems chosen for this investigation are n-heptane-toluene

and methylcyclohexane-toluene. They seem to be prototypes of two important classes of systems: aliphatic-aromatic and alicyclic-aromatic hydrocarbon mixtures. Such mixtures are of technical interest because they occur frequently in petroleum processing. The low freezing points of all components permit the determination of the excess thermodynamic properties over a wide temperature range. At room temperature, the systems n-heptane-toluene and methylcyclohexane-toluene show relatively high values of H^E, G^E, and S^E [25,40,44,45], whereas the system n-heptane-methylcyclohexane shows almost ideal behavior[9,25]. Mixtures composed of only saturated or only aromatic hydrocarbons generally deviate less from ideality than mixtures containing both types of components (see Reference 35, Chapter IV).

Since the four excess thermodynamic functions, G^E, H^E, S^E, and C_p^E, are related by thermodynamic equations (see Chapter V) it is sufficient to determine the temperature dependence of one of these properties in order to establish the temperature dependence of the other properties.

G^E is usually determined from vapor-liquid equilibria, a method which is not suitable for temperature regions where the vapor pressure of the mixture is very low. Also, the other excess functions would have to be obtained by differentiating G^E with respect to temperature, which introduces large uncertainties in the derived properties. H^E can be measured directly in a heat-of-mixing calorimeter. However, a large number of measurements would be required to cover a wide range of temperature and composition, resulting in a lengthy experimental program.

The method chosen for this work was to determine excess heat capacities by measuring the heat capacities of the pure components and several mixtures over a wide range of temperature and to obtain the other excess functions by integration, as shown in Chapter V.

Literature data on heat capacities of aliphatic-aromatic and alicyclic-aromatic mixtures are extremely scarce and of low accuracy. Since the excess heat capacity is usually small compared to the total heat capacity of the mixture, a small error in C_p will cause a large error in C_p^E. This is illustrated by the measurements of Atwood[5] on the system cyclohexane-benzene between the freezing point and 303.15 K. The excess heat capacity was found to have a minimum of -2.9 J/mole K on the benzene side and a maximum of 0.4 J/mole K on the cyclohexane side. Since the claimed accuracy is one per cent, or about 1.3 J/mole K, the measured values are of the same magnitude as the uncertainty of the measurement. Precise measurements of the heat of mixing for the system cyclohexane-benzene and a number of other aliphatic-aromatic and alicyclic-aromatic mixtures at 298.15 and 323.15 K[25] show that the mean excess heat capacity between these temperatures is always negative and shows a nearly quadratic dependence on composition. The S-shaped curve found by Atwood would therefore be highly unusual for this type of system. This example shows that precision calorimetry is required to obtain reliable excess heat capacity data.

Many workers have studied the excess enthalpies, free energies, and volumes of mixtures of saturated and aromatic hydrocarbons near room temperature. Most of the results have been summarized by Rowlinson (Reference 35, Chapter IV). The behavior of the system cyclohexane-

benzene is fairly typical for these mixtures. H^E is large and positive; both G^E and $T\,S^E$ are about half as large as H^E. All three excess functions decrease with increasing temperature. The excess volume is positive and independent of temperature between 293.15 and 343.15 K. All excess properties show a nearly quadratic dependence on composition.

Since both cyclohexane and benzene freeze at about 279 K and boil at about 353 K, the excess thermodynamic properties of their mixtures can only be studied over a limited temperature range. Although there are many hydrocarbons which have normal boiling points above room temperature and much lower freezing points than cyclohexane or benzene, it appears that mixtures of such hydrocarbons have not been studied below the ice point.

A number of theories have been used to interpret the observed excess thermodynamic properties of cyclohexane-benzene and related systems. Only theories based on statistical mechanics are considered here.

The simplest theory of liquid mixtures is the theory of strictly regular solutions, which has been described in detail by Guggenheim[16]. This model always predicts a very small, negative excess entropy and zero excess volume, in disagreement with experimental results on practically all types of mixtures. Guggenheim has shown that a positive excess entropy may be predicted if the intermolecular energies are assumed to be temperature-dependent. However, the theory gives no clue as to how these energies should vary with temperature.

An important class of theories is based on the cell model of the liquid state[3,31,38,42]. Most of these theories predict the

excess volume of the system benzene-cyclohexane fairly well, but the predicted excess entropy is only one-fourth to half of the experimental value. Flory[15] has published a theory based on a cell model which is not restricted to spherical molecules and which will therefore be used to correlate the results of this work (see Chapter VI). Abe and Flory[1] have tested this theory for a number of systems, including cyclohexane-benzene, n-hexane-benzene, and n-heptane-benzene. The predicted excess volumes are in good agreement with experiment, but the predicted excess entropies are too low, although higher than for most of the theories cited above.

Another group of theories is based on corresponding states principles, without using a model for the liquid state. The excess thermodynamic properties of a mixture are expressed in terms of the configurational properties of a reference substance. The simplest such theory is the first-order conformal solution theory of Longuet-Higgins[24], which assumes that the molecules are spherically symmetric. For the system benzene-cyclohexane, the theory predicts the excess volume fairly well, but the predicted excess entropy is too small.

Quantum mechanical calculations of the intermolecular forces between benzene molecules[6,32] show a strong dependence on orientation due to the influence of the π-electrons. Similar effects are to be expected in other aromatic liquids, like toluene. Scatchard et al.[39] already suggested that the large positive excess entropy of the system cyclohexane-benzene is due to a preferred orientation of the molecules in one or both of the components. Rowlinson and Sutton[37] have extended the conformal solution theory to molecules whose potentials depend on

orientation. They applied their theory to the excess thermodynamic functions of an equimolar mixture of cyclohexane and benzene at 298.15 and 343.15 K and obtained excellent agreement with experiment. The much longer temperature range covered by the data on n-heptane-toluene and methylcyclohexane-toluene reported in this work should provide an excellent test for the theory of Rowlinson and Sutton, as well as for the original conformal solution theory of Longuet-Higgins. Both theories are therefore used to correlate the results of this work (see Chapter VI).

CHAPTER II

EXPERIMENTAL APPARATUS AND PROCEDURE

Description of the Calorimeter

The heat capacity measurements were carried out in a precision adiabatic-shield, high-vacuum calorimeter which has been described in detail by McGee[28] and which has been used by McGee[28], Hwa and Ziegler[18, 19], Liu and Ziegler[22,23], and by Brown[10]. Only a brief description will be given here.

Figure 1 shows a schematic diagram of the calorimeter. The sample is contained in a gold-plated copper can equipped with a constantan heater and a platinum resistance thermometer (Leeds and Northrup No. 1048215) which has been calibrated by the National Bureau of Standards (see Appendix A). The two filling ports of the can are sealed with soft soldered caps. The can is suspended from a fine wire within a light-weight copper shield. The temperature difference between can and shield is monitored by thermocouples. Heater wires are wrapped around the outside of the shield, and by manually adjusting the power input into these heaters the temperature difference between can and shield can be made very small, thus minimizing radiation losses. The shield is suspended from a ring which is also equipped with a heater and thermocouple indicating the temperature difference between the ring and the top of the shield. By making this temperature difference very small, conductive losses through the wires are kept at a minimum.

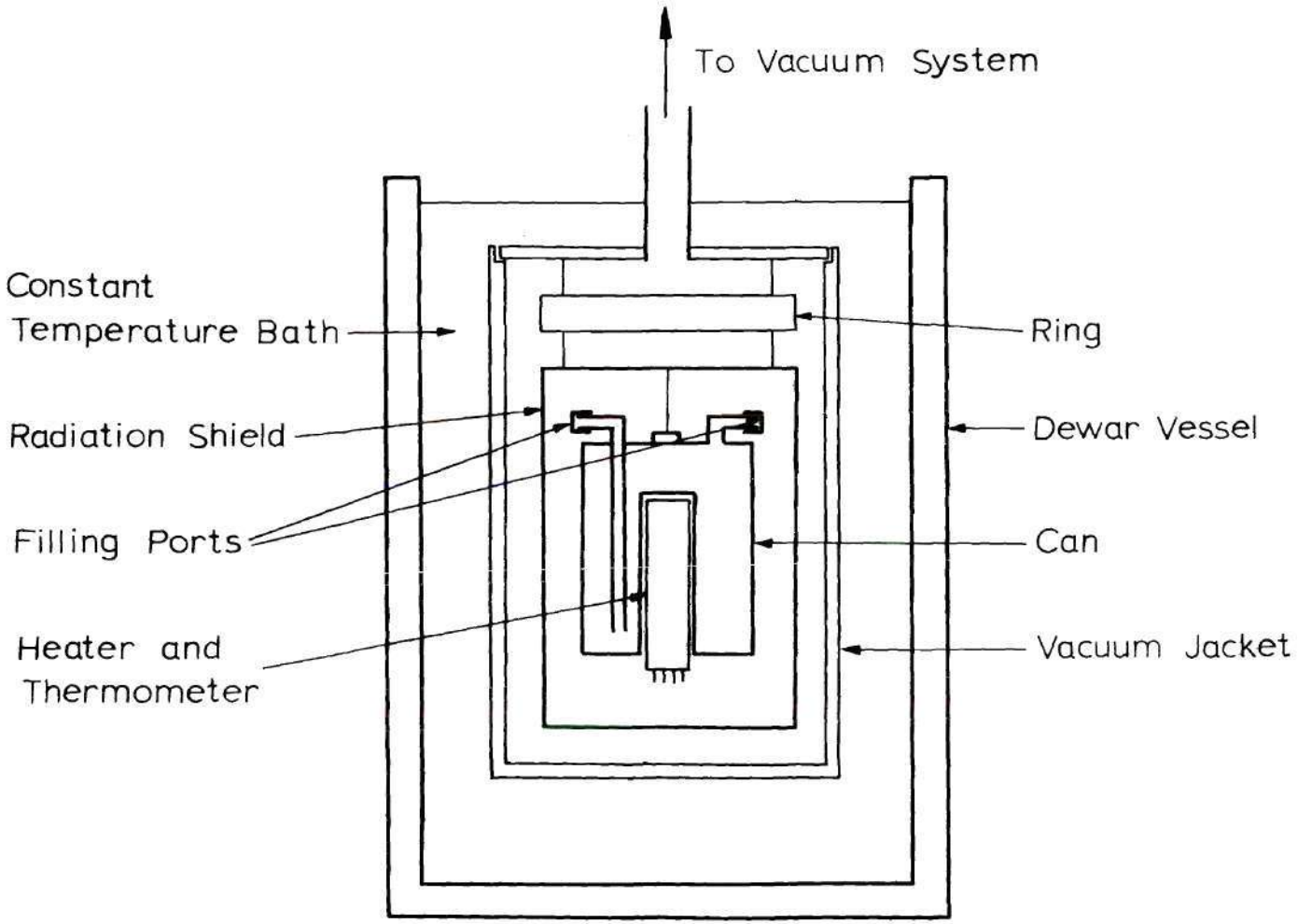


Figure 1. Schematic Diagram of the Calorimeter

The whole assembly is suspended from thin wires within a vacuum jacket which is supported by a thin-wall monel tube. This tube contains the electric leads and also serves as a pumping line for the high-vacuum system. The vacuum jacket is immersed in a constant-temperature bath which is at the same or (usually) a lower temperature than the can.

The energy for the calorimeter heater is furnished by a Hewlett-Packard 6101 A DC Power Supply. In order to keep steady load conditions, a ballast heater is connected to the power supply whenever the calorimeter heater is not in use. The potentials across the heater and across a one-ohm standard resistor are measured with a Leeds and Northrup 100,000 μV White Double Potentiometer. Since the potential across the calorimeter heater is too high to be measured directly it is reduced by a volt box. The resistors and standard cells used were calibrated by the National Bureau of Standards. The heating interval is measured with a 110 V, 60 cycle timer (Standard Electric Timer Co., Springfield, Mass.). The resistance of the thermometer is measured with a Leeds and Northrup Mueller G-2 resistance bridge. The shield and ring heaters are powered by a 110 V AC source, with the voltage suitably reduced by manually operated variable transformers and resistors.

Experimental Procedure

The weight of the empty can was determined on a balance which was accurate to about 5 mg. The sample liquid was then transferred to the can by means of a filling bottle with a marked volume of about

150 cm^3. All liquid transfers were carried out by exerting dry nitrogen pressure. Since the volume of the calorimeter can was about 160 cm^3, a gas space of about 10 cm^3 remained above the liquid. The can was then weighed, sealed, and weighed again. It was suspended in the calorimeter, the heater and thermometer wires were connected by soldering and tested for correct hookup and possible shorts. The shields were then replaced, the vacuum jacket was soldered and checked for vacuum tightness.

Four different constant temperature baths were used: a liquid nitrogen bath for the temperature range below about 201 K; an ethanol-solid CO_2 bath from about 195 to 279 K; an ice bath from about 273 to 298 K; and a water bath from about 282 to 312 K. There was always an overlap of about six degrees between adjacent temperature ranges to verify that the change in bath temperature did not have a significant influence on the heat capacity results. The calorimeter was cooled down by admitting helium gas into the jacket. At the desired temperature the helium gas was pumped out, and the system was evacuated to about 10^{-5} Torr.

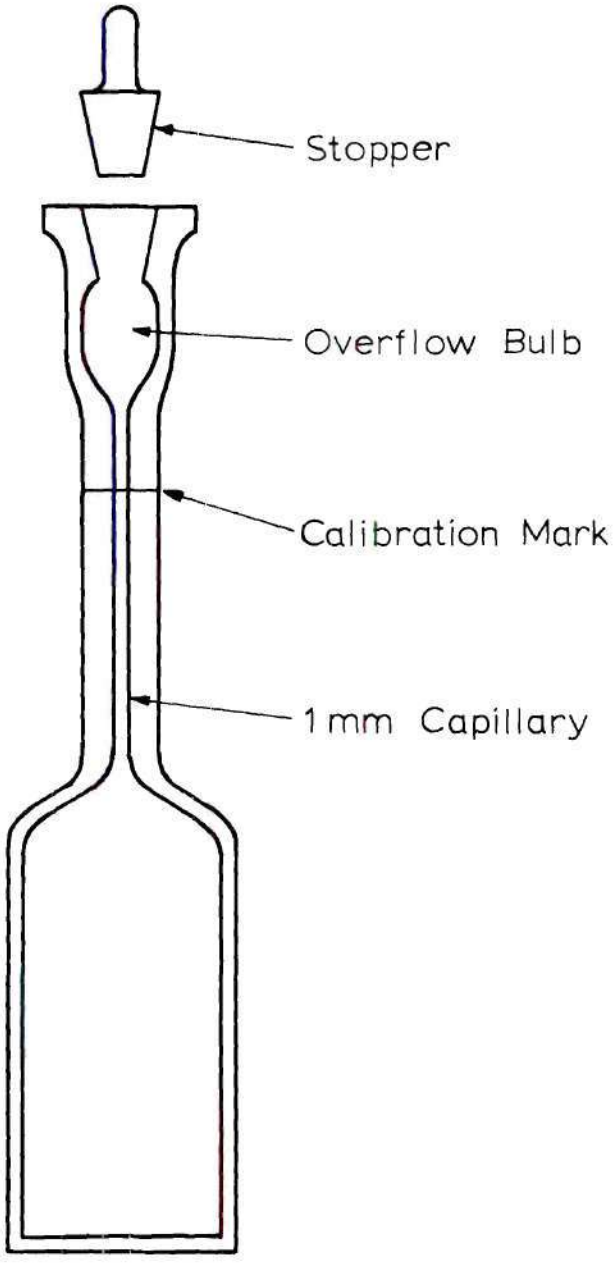
In a heat capacity measurement, the shields and the ring were first brought to the same temperature as the can, and the temperature was measured repeatedly until steady. The calorimeter heater was switched on, which also automatically started the timer, and the shields were again brought into balance. The voltages across the calorimeter heater and across the standard resistor were recorded after approximately 1/4 of the total heating time had elapsed, and again after approximately 3/4 of the heating time. The heater was

then switched off, which also stopped the timer. The shields were balanced again, and the temperature was recorded until steady. The measurements were mostly carried out continuously, with the final temperature of one measurement being the starting temperature of the next one. The temperature increment was always about five degrees, with heating times of 14 to 25 minutes and equilibrium periods of 20 to 25 minutes. Measurements in the melting region were carried out like heat capacity measurements, except that the heating and equilibrium periods were longer, up to 90 and 180 minutes, respectively.

Density Measurements

Liquid density measurements were carried out in a single-stem, Bingham-type pycnometer (shown in Figure 2) following essentially the procedure recommended by the American Society for Testing and Materials[4].

In a density measurement, the empty pycnometer was first rinsed with acetone and vacuum dried. If the inside of the pycnometer did not appear to be perfectly clean after drying, it was cleaned with chromic acid, rinsed with distilled water and acetone, and vacuum dried. The average weight of the empty pycnometer was found to be 28.1797 g. Individual weighings never deviated by more than 0.2 mg from this value. All weighings were carried out on a precision laboratory balance (Becker Chainomatic No. 43531). The weights used were manufactured by Ainsworth and Son, Denver, Colo. According to the manufacturer, the actual weights agree with the nominal weights within 0.05 mg. All weighings were carried out twice, with the pycnometer first on one and then the other balance pan, in order to eliminate corrections for



Material: Borosilicate Glass

Figure 2. Bingham Pycnometer

zero point and unequal beam length. The average of both weighings was used and corrected for buoyancy.

The volume of the pycnometer was determined using freshly boiled, distilled water which had been redistilled from $KMnO_4$. The pycnometer was filled using a stainless steel transfer tube which fitted into the capillary of the pycnometer. It was filled sufficiently high above the calibration mark to allow for any thermal contraction of the liquid.

The pycnometer was then immersed into a thermostated stirred water bath contained in a Dewar vessel. The temperature was maintained at 293.15 K by a Sargent "Thermonitor" controller equipped with a thermistor sensor and a heater with a maximum power of 300 W. Cooling was provided by passing tap water through a coil immersed in the bath. The temperature was monitored to 0.001 degrees using a platinum resistance thermometer (Leeds and Northrup No. 709892) calibrated by the National Bureau of Standards (see Appendix A) and was maintained within $\pm$ 0.005 degrees.

After about five minutes, excess liquid was withdrawn from the pycnometer with a microliter syringe to bring the meniscus down to a few mm above the calibration mark. After about another five minutes, no further motion of the meniscus was observed, indicating that the pycnometer had come to thermal equilibrium. However, the pycnometer was left in the bath for a total of at least 30 minutes. Then enough liquid was withdrawn to make the bottom of the meniscus coincide exactly with the calibration mark. The upper part of the capillary and the overflow reservoir were then carefully dried with pipe cleaners. The

pycnometer was stoppered up, removed from the bath, dried on the outside and allowed to equilibrate in the balance for about 30 minutes prior to weighing. From the weight difference between the full and empty pycnometer and the known density of water at 293.15 K[4], the volume of the pycnometer was determined as 23.4655 cm^3 (average of four runs). Using this value, the densities of the pure liquids and the mixtures were determined by the same method as used for the calibration. Three measurements were made for each component and two for each mixture. In a given set of measurements, the weight of the full pycnometer never varied by more than $\pm$ 0.2 mg. The densities were determined at the same mixture compositions as the heat capacities.

The liquid densities are estimated to be accurate to 0.00003 g/cm^3.

CHAPTER III

MATERIALS AND PURIFICATION

Source and Purification

All samples were obtained from the Phillips Petroleum Company. The methylcyclohexane was Research Grade (Lot No. 1291) and was used without purification. The purity of the lot (by freezing point determination) was stated to be 99.86 mole per cent, and the impurities detected by GLC analysis were stated to be cis-1,2-dimethylcyclopentane, 2,2-dimethylcyclohexane, and toluene. The n-heptane and toluene were Pure Grade (n-heptane: Lot No. 1312, toluene: Lot No. R-529), and the purity was stated to be at least 99 mole per cent. They were purified by fractional distillation in a strip-silvered, vacuum-jacketed column having a five-foot section packed with glass helices. The distillation was carried out under atmospheric pressure using a reflux ratio of about 10:1.

Impurity and Melting Point Determination

The impurity content of the samples before and after purification and the melting points of the pure materials were determined using the calorimeter according to a method outlined by Rossini[34].

The sample material was cooled down by surrounding the vacuum jacket with liquid nitrogen and introducing a sufficient amount of helium into the jacket to cool the sample at a rate of about 6 K/hr. The methylcyclohexane and toluene started freezing about 8 and 19 degrees,

respectively, below their nominal freezing points. The start of the freezing process was characterized by a sharp rise in temperature. The n-heptane showed no significant supercooling before freezing.

The melting process was carried out in the same manner as the heat capacity measurements. At least four equilibrium points in the melting region and at least one in the liquid region were obtained.

If the enthalpy of the pure solid at the melting point, T_m, of the pure substance is arbitrarily set equal to zero, the enthalpy of the liquid after the last heat input (at the temperature T_1) is

$$\tilde{H}(T_1) = \tilde{H}_f + \int_{T_m}^{T_1} \tilde{C}_{p\ \text{liquid}}\, dT \qquad (1)$$

where $\tilde{H}_f$ denotes the heat of fusion of the pure material. Once $\tilde{H}(T_1)$ is known, the enthalpy at any equilibrium point in the melting region can be determined from the known amount of heat put into the sample (after correcting for the heat capacity of the can). On the other hand, the enthalpy corresponding to a certain fraction melted, x, is given by

$$\tilde{H} = (1 - x) \int_{T_m}^{T} \tilde{C}_{p\ \text{solid}}\, dT + x \left(\tilde{H}_f + \int_{T_m}^{T} \tilde{C}_{p\ \text{liquid}}\, dT\right) \qquad (2)$$

The heat capacities can be assumed to be independent of temperature in the range considered. The values for $\tilde{H}_f$, T_m, $\tilde{C}_{p\ \text{solid}}$, and

$\tilde{C}_{p\ liquid}$ can be taken from the literature since the calculation is not very sensitive to any errors in these quantities. From equation (2), the fraction melted can be calculated as

$$x = \frac{\tilde{H} + (T_m - T)\,\tilde{C}_{p\ solid}}{\tilde{H}_f - (T_m - T)(\tilde{C}_{p\ liquid} - \tilde{C}_{p\ solid})} \qquad (3)$$

Assuming that all the impurity stays in the liquid phase and forms an ideal solution, it can be shown that a plot of 1/x vs. T yields a straight line which can be extrapolated to 1/x = 0. The temperature corresponding to that point is the melting point, T_m, of the pure material. The mole fraction, x_2, of the impurity can be calculated from the slope of the line

$$x_2 = \frac{\tilde{H}_f}{RT_m^2} \frac{dT}{d(1/x)} \qquad (4)$$

Table 1 lists the literature values for T_m, $\tilde{H}_f$, $\tilde{C}_{p\ liquid}$, and $\tilde{C}_{p\ solid}$ used in the calculation. The results of the melting point and impurity determinations are listed in Table 2.

Using an identical technique, Brown[10] determined the impurity of the n-heptane sample before distillation as 0.30 ± 0.08 mole per cent. After distillation, an impurity content of 0.27 ± 0.10 mole per cent was found, which is no significant improvement. The impurity of the toluene sample was reduced to about half its original amount by distillation.

Comparison of Melting Points with Literature Data

The comparisons are made on the basis of the International

Table 1. Literature Data Used in Melting Point Determination

Material	T_m, K (IPKS-54)*	$\tilde{H}_f$ J/mole	$\tilde{C}_{p\ liquid}$ J/mole K	$\tilde{C}_{p\ solid}$ J/mole K	Source
n-Heptane	182.55	14037	203.01	146.59	McCullough and Messerly[27]
Methyl-cyclohexane	146.57	6750	139.20	90.63	Douslin and Huffman[13]
Toluene	178.15	6636	135.44	89.57	Scott et al.[41]

*See Appendix A for definition of temperature scales

Practical Kelvin Scale of 1954 (IPKS-54, see Appendix A). The melting points of this work were determined under a pressure of roughly 0.5 atm. Since the pressure effect on the melting point below atmospheric pressure is usually less than the uncertainty of the melting point, no corrections have been made when comparing the results of this work with melting points and triple points reported in the literature.

McCullough and Messerly[27] give 182.55 $\pm$ 0.01 K for the melting point of n-heptane. Douglas et al.[12] report 182.55 $\pm$ 0.01 K*, and Brown[10] gives 182.562 $\pm$ 0.04 K. The API Tables[2] list 182.55 K for the triple point temperature. The melting point reported here agrees with all these measurements within 0.01 K.

The melting point of methylcyclohexane has been determined by Douslin and Huffman[13] and Hwa[18], who give 146.57 $\pm$ 0.05 K* and 146.65

*The original value has been lowered by 0.01 degrees to conform with the definition of the IPKS-54.

Table 2. Summary of Purity and Melting Point Determinations

n-Heptane		
Fraction Melted	Temperature, K (IPKS-68)*	Mole Fraction Impurity
0.30744	182.409	0.00275
0.50725	182.485	0.00259
0.70743	182.512	0.00264
0.90782	182.524	0.00281
Melting Point of Pure n-Heptane	182.586 ± 0.030 K (IPKS-68) 182.557 ± 0.030 K (IPKS-54)*	
Mole Fraction Impurity	0.0027 ± 0.0010	

Methylcyclohexane		
Fraction Melted	Temperature, K (IPKS-68)	Mole Fraction Impurity
0.27630	146.431	0.00121
0.45286	146.474	0.00124
0.59382	146.493	0.00120
0.77144	146.504	0.00125
0.91248	146.516	0.00107
Melting Point of Pure Methylcyclohexane	146.550 ± 0.030 K (IPKS-68) 146.554 ± 0.030 K (IPKS-54)	
Mole Fraction Impurity	0.0012 ± 0.0005	

* See Appendix A for Definition of Temperature Scales

Table 2 - continued

Toluene (Before Purification)		
Fraction Melted	Temperature, K (IPKS-68)	Mole Fraction Impurity
0.16795	176.979	0.00495
0.40772	177.679	0.00484
0.65787	177.855	0.00488
0.91006	177.927	0.00510
Melting Point of Pure Toluene	178.150 ± 0.050 K (IPKS-68)	
	178.124 ± 0.050 K (IPKS-54)	
Mole Fraction Impurity	0.0050 ± 0.0010	

Toluene (After Purification)		
Fraction Melted	Temperature, K (IPKS-68)	Mole Fraction Impurity
0.20663	177.688	0.00247
0.42147	177.937	0.00242
0.67084	178.024	0.00240
0.92134	178.055	0.00257
Melting Point of Pure Toluene	178.166 ± 0.030 K (IPKS-68)	
	178.140 ± 0.030 K (IPKS-54)	
Mole Fraction Impurity	0.0024 ± 0.0010	

$\pm$ 0.10 K, respectively. The API Tables list 146.57 K for the triple point. The sample used by Hwa had a purity of only 99 mole per cent, which explains the large uncertainty of his melting point temperature. The melting point determined in this work agrees with the values given by Douslin and Huffman and the API Tables within 0.02 K.

The melting point of toluene has been measured by Scott et al.[41] and by Hwa[18]. Their values are 178.15 $\pm$ 0.05 K and 178.159 $\pm$ 0.02 K, respectively. The API Tables give 178.15 K for the triple point. The melting point of toluene (after purification) determined in this work agrees with all these values within 0.02 K.

CHAPTER IV

EXPERIMENTAL RESULTS

Calculation of the Heat Capacity from Experimental Data

The heat capacity of the sample is computed from the formula

$$\tilde{C}_p = H_s/n(T_2 - T_1) \tag{5}$$

where T_1 and T_2 are the initial and final temperatures of the measurement, respectively, and n is the number of moles of sample. The heat input into the sample, H_s, is determined from the relation

$$H_s = H - H_c \tag{6}$$

H is the total heat input into the can, which is determined from the potential readings across the calorimeter heater and the standard resistor, and from the heating time. H_c is the heat absorbed by the can alone, which is computed from the heat capacity of the empty can given by Hwa[18]. A sample calculation of the heat capacity of a mixture and a discussion of various sources of error are given in Appendix B.

The sample compositions and the temperature range of the measurements are summarized in Table 3. The experimental heat capacity data for the pure components and their mixtures are given in Table 8, Appendix C. They are based on the International Practical Kelvin Scale of 1968 (IPKS-68, see Appendix A). For comparison with literature data, the heat capacities of the pure components were also computed using the

Table 3. Sample Composition and Temperature Range of Heat Capacity and Density Measurements

System	Composition x_1	Temperature Range of $\tilde{C}_p$ Measurements K	Temperature of Density Measurements K
n-Heptane		182-312	293.15
Methylcyclohexane		144-312	293.15
Toluene		162-312	293.15
n-Heptane(1)-Toluene	0.18810	182-312	293.15
n-Heptane(1)-Toluene	0.34751	182-312	293.15
n-Heptane(1)-Toluene	0.50341	182-312	293.15
n-Heptane(1)-Toluene	0.66119	182-312	293.15
n-Heptane(1)-Toluene	0.82359	182-312	293.15
Methylcyclohexane(1)-Toluene	0.16728	162-312	293.15
Methylcyclohexane(1)-Toluene	0.31372	162-312	293.15
Methylcyclohexane(1)-Toluene	0.53541	162-312	293.15
Methylcyclohexane(1)-Toluene	0.66700	162-312	293.15
Methylcyclohexane(1)-Toluene	0.82676	162-312	293.15
n-Heptane(1)-Methylcyclohexane	0.48910	182-312	293.15

International Kelvin Scale of 1954 (IPKS-54). The heat capacities of the pure components were fitted by polynomials using the method of least squares. The quality of these fits can be judged by the sum of the squares of the residuals, y, or the standard deviation, z, which are defined by the following relations

$$y = \sum [\tilde{C}_p(\text{calculated}) - \tilde{C}_p(\text{experimental})]^2 \quad (7)$$

$$z = \sqrt{y/(n - m)} \quad (8)$$

where m and n denote the number of constants used in the fit and the

number of data points, respectively.

The coefficients of the polynomials and the standard deviation are given in Table 9, Appendix C. Apart from a few exceptional points, the polynomials represent the experimental data within 0.1 per cent.

Discussion of the Heat Capacity Data

Table 10, Appendix C, gives a comparison of the heat capacities of the pure components with literature data of high quality, based on the International Practical Kelvin Scale of 1954 (IPKS-54). The heat capacity values of this work were computed from the polynomials given in Table 9, Appendix C. Literature data were taken from the tables of smoothed values given in the original papers. If no smoothed data were given, heat capacities were computed from the polynomials given in the papers.

A comparison of the heat capacity of n-heptane shows that the results of this work are about 0.15 to 0.35 per cent lower than the data of McCullough and Messerly[27] and about 0.05 to 0.25 per cent lower than the data of Douglas et al.[12] Both McCullough and Messerly and Douglas et al. claim an accuracy of 0.1 per cent. The discrepancy could at least partly be attributed to the impurity in the n-heptane sample used in this work (0.27 mole per cent). The agreement with the data of Brown[10], who used the same calorimeter and essentially the same sample (see Chapter III), and who claims an accuracy of 0.2 per cent, is very good, except for the room temperature region, where Brown's values are up to 0.2 per cent higher than the results of this work. This may be due to the fact that in this work a water bath at

293 K was used for the upper room temperature range, whereas Brown used an ice bath at 273.15 K for the same temperature range. A large temperature difference between shield and bath means a large radiation loss from the shield, which increases any errors caused by uneven temperature distribution on the shield. Therefore the measurements using a water bath seem to be more reliable than measurements using an ice bath for the same temperature range.

The heat capacity of methylcyclohexane has been measured by Douslin and Huffman[13], and by Hwa[18]. Both claim an accuracy of 0.2 per cent. The agreement with the data of Douslin and Huffman is good, with an average deviation of about 0.1 per cent and a maximum deviation of less than 0.2 per cent. The data reported by Hwa are consistently about 0.15 per cent higher than the data reported in this work. This discrepancy may be due to a failure by Hwa to include the buoyancy correction for the sample weight, which would lower his heat capacity values by about 0.14 per cent, in perfect agreement with the results of this work.

The heat capacity of toluene was measured by Scott et al.[41] and by Hwa[18]. Both claim an accuracy of 0.2 per cent. The agreement with the data of Scott et al. is good between about 200 and 280 K, but at the highest and lowest temperatures of measurement, the values of Scott et al, are up to 0.25 per cent higher than the data reported here. The data of Hwa are, on the average, about 0.1 per cent higher than the results of this work. An inclusion of the buoyancy correction would lower his values by about 0.12 per cent, making the agreement even better.

The comparison with literature data shows that the data reported here generally agree well with data of other workers using precision calorimeters. Some disagreement in the case of n-heptane may be due to the impurity in the sample. The agreement with the data of Brown and Hwa, which were measured with the same calorimeter as used in this work, suggests that the performance of the calorimeter has not changed appreciably since the time of these measurements. It is therefore concluded that the accuracy of the heat capacity data is 0.2 per cent, the same accuracy as claimed by Hwa and Brown.

Densities

The measured densities of the pure components at 293.15 K and the corresponding values given in the API Tables[2] are listed in Table 4. The measured density of methylcyclohexane agrees with the API value within the uncertainty of the measurement ($\pm$ 0.00003 g/cm^3). The measured densities of the n-heptane and toluene samples are 0.00011 g/cm^3 higher and 0.00048 g/cm^3 lower, respectively, than the corresponding API values. Since these differences exceed the uncertainty of the measurement they are attributed to the impurity content in the samples.

Table 4. Densities of the Pure Components at 293.15 K

Component	Density, g/cm^3	
	This Work	API[2]
n-Heptane (after purification)	0.68387	0.68376
Methylcyclohexane	0.76941	0.76939
Toluene (after purification)	0.86648	0.86696

CHAPTER V

DERIVED EXCESS THERMODYNAMIC PROPERTIES

Method of Deriving the Excess Thermodynamic Properties

The excess thermodynamic properties, $\tilde{G}^E$, $\tilde{H}^E$, $\tilde{S}^E$, $\tilde{C}_p{}^E$, and $\tilde{V}^E$, of a binary liquid mixture are defined by the following relations:

$$\begin{aligned}\tilde{G}^E &= [\tilde{G} - (x_1 \tilde{G}_1 + x_2 \tilde{G}_2) - R T (x_1 \ln x_1 + x_2 \ln x_2)]_{P,T} \\ &= [\tilde{G}^M - R T (x_1 \ln x_1 + x_2 \ln x_2)]_{P,T}\end{aligned} \tag{9}$$

$$\tilde{H}^E = [\tilde{H} - (x_1 \tilde{H}_1 + x_2 \tilde{H}_2) = \tilde{H}^M]_{P,T} \tag{10}$$

$$\begin{aligned}\tilde{S}^E &= [\tilde{S} - (x_1 \tilde{S}_1 + x_2 \tilde{S}_2) + R (x_1 \ln x_1 + x_2 \ln x_2)]_{P,T} \\ &= [\tilde{S}^M + R (x_1 \ln x_1 + x_2 \ln x_2)]_{P,T}\end{aligned} \tag{11}$$

$$\tilde{C}_p{}^E = [\tilde{C}_p - (x_1 \tilde{C}_{p1} + x_2 \tilde{C}_{p2}) = \tilde{C}_p{}^M]_{P,T} \tag{12}$$

$$\tilde{V}^E = [\tilde{V} - (x_1 \tilde{V}_1 + x_2 \tilde{V}_2) = \tilde{V}^M]_{P,T} \tag{13}$$

The quantities, $\tilde{G}^E$, $\tilde{H}^E$, $\tilde{S}^E$, and $\tilde{C}_p{}^E$, are related by the following equations:

$$\left[\frac{\partial(\tilde{G}^E/T)}{\partial T} = -\frac{\tilde{H}^E}{T^2}\right]_{P,x} \tag{14}$$

$$\left[\frac{\partial \tilde{H}^E}{\partial T} = \tilde{C}_p{}^E\right]_{P,x} \tag{15}$$

$$[T \tilde{S}^E = \tilde{H}^E - \tilde{G}^E]_{P,T,x} \tag{16}$$

Equations (14), (15), and (16) are sufficient for the derivation given below. However, two more equations are given here to show how $\tilde{S}^E$ is directly related to $\tilde{G}^E$ and $\tilde{C}_p{}^E$:

$$\left[\frac{\partial \tilde{G}^E}{\partial T} = - \tilde{S}^E \right]_{P,x} \tag{17}$$

$$\left[\frac{\partial \tilde{S}^E}{\partial T} = \frac{\tilde{C}_p{}^E}{T} \right]_{P,x} \tag{18}$$

If $\tilde{G}^E$ and $\tilde{H}^E$ are known at one (not necessarily the same) temperature, T_o, they can be computed within the temperature range of the excess heat capacity data by integration of Equations (14) and (15):

$$\left[\tilde{H}^E(T) = \tilde{H}^E(T_o) + \int_{T_o}^{T} \tilde{C}_p{}^E(T)\, dT\right]_{P,x} \tag{19}$$

$$\left[\tilde{G}^E(T) = \frac{T}{T_o} \tilde{G}^E(T_o) - T \int_{T_o}^{T} \frac{\tilde{H}^E}{T^2}\, dT\right]_{P,x} \tag{20}$$

$\tilde{S}^E$ can be calculated from $\tilde{G}^E$ and $\tilde{H}^E$ using Equation (16). Activity coefficients are computed from the relations:

$$\left[R\ T\ \ln\ \gamma_1 = \tilde{G}^E + x_2 \frac{\partial \tilde{G}^E}{\partial x_1}\right]_{P,T} \tag{21}$$

$$\left[R\ T\ \ln \gamma_2 = \tilde{G}^E - x_1 \frac{\partial \tilde{G}^E}{\partial x_1}\right]_{P,T} \tag{22}$$

Derivation and Fit of the Excess Heat Capacity

The experimental heat capacity data of the pure components and their mixtures were generally not determined at exactly the same temperatures. In order to apply Equation (12), the heat capacities of the pure components were computed from the polynomials given in Table 9, Appendix C. The derived excess heat capacities are listed in Table 8, Appendix C.

The excess heat capacity data must be fitted in some functional form to derive the other excess properties. One possible way is to fit the data individually for each mixture as functions of temperature. Equations (19), (20), and (16) can then be used to derive the other excess functions at the compositions of these mixtures. In order to determine the excess properties at other compositions and to compute partial molar quantities, the excess properties are fitted at selected temperatures as functions of composition. This method has been used by Hwa[18] and Brown[10] to fit the excess properties of alcohol-hydrocarbon systems, which deviate far from a quadratic dependence on composition.

An alternate method is to fit the excess heat capacity data for all mixtures of one system to a common function of temperature and composition. The derived excess properties are then also obtained as functions of both temperature and composition. This second method was chosen because it is mathematically more elegant, greatly reduces the number of constants required, and permits computation of excess thermodynamic functions and partial molar quantities at any desired composition.

The function used for the fit of the $\tilde{C}_p^E$ data is

$$\tilde{C}_p^{\,E} = x_1\, x_2\, [A_o(T) + A_1(T)(x_1 - x_2) + A_2(T)(x_1 - x_2)^2 + \ldots] \quad (23)$$

It corresponds to the equation proposed by Redlich and Kister[33] for representing excess thermodynamic functions, except that the coefficients A_o, A_1, and A_2 are here, in general, functions of temperature.

If all coefficients in Equation (23) except A_o were zero, all points in a plot of $\tilde{C}_p^{\,E}/x_1x_2$ should fall on a common curve. However, such plots show systematic deviations with composition for both systems. Since these deviations, which represent contributions of the higher coefficients, are relatively small, these coefficients were assumed to be independent of temperature. A_o was represented by a polynomial of the form

$$A_o(T) = a_o + a_1\, T + a_2\, T^2 + a_3\, T^3 \quad (24)$$

Three fits were attempted, one using only the coefficient A_o, one including A_o and A_1, and one using A_o, A_1, and A_2. The numerical values of the coefficients were determined by minimizing the sum of the squares of the residuals,

$$y = \sum [\tilde{C}_p^{\,E}(\text{calculated}) - \tilde{C}_p^{\,E}(\text{experimental})]^2 \quad (25)$$

The quality of the fits was judged by the standard deviation, which is defined by Equation (8).

Table 5 shows that the quality of the fits improves substantially through the introduction of the higher coefficients A_1 and A_2. The fits using A_o, A_1, and A_2 were selected for both systems because a standard deviation of about 0.1 J/mole K (corresponding to about 2 to 18 per cent

Table 5. Quality of Various $\tilde{C}_p^E$ Fits

Coefficients Used in Equation (23)	Standard Deviation J/mole K
System n-Heptane-Toluene	
A_o	0.2048
A_o, A_1	0.1075
A_o, A_1, A_2	0.0992
System Methylcyclohexane-Toluene	
A_o	0.1479
A_o, A_1	0.1442
A_o, A_1, A_2	0.1007

of the excess heat capacity data and to about 0.05 to 0.07 per cent of the total heat capacity) seems very satisfactory. In view of this fact, fits using constants higher than A_2 were not attempted.

The equations representing $\tilde{C}_p^E = f(T,x)$ are given in Table 13, Appendix E.

Literature Data Used

System n-Heptane-Toluene

Enthalpies of mixing have been measured by Lundberg[25] at 298.15 and 323.15 K, by Mathieson and Thynne[26] at 293.15 K, and by Tsao and Smith[46] at 298.15 K. Lundberg and Tsao and Smith claim accuracies of one and two per cent, respectively. However, their smoothed data at 298.15 K differ by about six per cent. The data of Mathieson and Thynne lie between these two curves (ignoring the small temperature dependence

between 293.15 and 298.15 K). The authors claim an accuracy of 0.7 per cent, which seems optimistic considering the scatter of their data. Lundberg's data at 298.15 K were selected as integration constants because of their small scatter. The good internal consistency of Lundberg's data is further evidenced by the fact that the excess enthalpy at 323.15 K derived from these data at 298.15 K and from an extrapolation of the excess heat capacity determined in this work agrees with his measurements at 323.15 K within one per cent.

Vapor-liquid equilibria have been measured at 298.15 K by Katayama et al.[20] and by Surovy and Heinrich[45]. Because of the low pressures (below 50 Torr) no corrections were applied for the imperfection of the vapor. Although the scatter of the data of Katayama et al. is extremely large, the smoothed $\tilde{G}^E$ curves differ only by about eight per cent. The results of Surovy and Heinrich were chosen as integration constants.

System Methylcyclohexane-Toluene

Excess enthalpies have been measured by Kuespert[21] at 293.15 K and by Sosnkowska-Kehiahian[44] at 283.15 and 298.15 K. Kuespert claims an accuracy of 0.6 per cent, which seems optimistic considering the scatter of his data. Sosnkowska-Kehiahian claims an accuracy of 20 J/mole, which corresponds to about four per cent of $\tilde{H}^E$ for the equimolar mixture. However, Kuespert's values are about 10 per cent lower than the data of Sosnkowska-Kehiahian at 293.15 K (interpolated from the measurements at 283.15 and 298.15 K). The data of Sosnkowska-Kehiahian at 283.15 K were selected because of their low scatter. The $\tilde{H}^E$ values at 298.15 K derived from these data and the excess heat

capacities determined in this work agree with the smoothed experimental data at 298.15 K within two per cent. The agreement is not as good as in the case of Lundberg's data for n-heptane-toluene, but is still satisfactory.

The only isothermal vapor-liquid equilibrium measurements for methylcyclohexane-toluene have been reported by Schneider[40] at 333.15; 353.15; 363.15; and 373.15 K. Since the heat capacity measurements only cover the range up to 312 K, they had to be extrapolated up to 333.15 K (see Appendix D). The internal consistency of Schneider's data is very good and supports his claim that they are accurate to one per cent. Corrections for the imperfection of the vapor were applied in deriving the excess free energies. $\tilde{G}^E$ data at 373.15 K which are based on the measurements at 333.15 K and an extrapolation of the excess heat capacity agree with the measurements taken at 373.15 K within about three per cent (see Table 14, Appendix E), which is very good considering that the $\tilde{C}_p^E$ values were extrapolated by more than 60 degrees.

System n-Heptane-Methylcyclohexane

Excess enthalpies have been measured by Cruetzen et al.[11] at 293.15 K, by Brandt[8] at 293.15 K, and by Lundberg[25] at 298.15 and 323.15 K. Brandt also measured $\tilde{H}^E$ at various temperatures between 285.85 and 313.05 K for a mixture containing 44.4 mole per cent n-heptane. He fitted these values by a straight line which yields an excess enthalpy of 18 J/mole at 298.15 K and -3 J/mole at 323.15 K (extrapolated). The corresponding values from a fit of Lundberg's data are about 34 and 19 J/mole, respectively. The values given by

Cruetzen et al. are somewhat higher than Brandt's data, and their scatter is relatively large. Lundberg's data were selected because of their good internal consistency. For the mixture composition of this work (0.48910 mole per cent n-heptane), the difference between the excess enthalpy at 323.15 K derived from Lundberg's measurements at 298.15 K and the extrapolated $\tilde{C}_p^E$ data, and the value taken from a fit of Lundberg's measurements at 323.15 K, is only 0.3 J/mole.

Vapor-liquid equilibria have been measured by Brandt and Roeck[9]. They found that, within the accuracy of the measurements, the mixture obeyed Raoult's law over the whole concentration range at 304.65; 320.64; and 353.10 K. From this they concluded that the excess free energy is 0 ± 4 J/mole over the whole range of the measurements. For the calculations, $\tilde{G}^E$ was taken as zero at 304.65 K.

Fit of the Selected Literature Data

The selected literature data were fitted by Redlich-Kister equations,

$$\tilde{E}^E = x_1 x_2 [C_o + C_1(x_1 - x_2) + C_2(x_1 - x_2)^2] \qquad (26)$$

using the method of least squares. (E stands for any extensive thermodynamic property.) The constants used in the fits and the standard deviation, which is defined by Equation (8), are listed in Table 6.

Excess Volumes

From the measured liquid densities, molar volumes were computed using the relation

$$\tilde{V} = (x_1 M_1 + x_2 M_2)/\rho \qquad (27)$$

Table 6. Constants Used in Fitting Selected Literature Data by Redlich-Kister Equations

Quantity Fitted	T	C_o	C_1	C_2	z*	Reference
	K	J/mole	J/mole	J/mole	J/mole	
			System n-Heptane-Toluene			
$\tilde{G}^E$	298.15**	1177.99	-95.78	0.00	11.51	45
$\tilde{H}^E$	298.15**	2209.07	-348.89	114.84	0.92	25
$\tilde{H}^E$	323.15	2094.90	-315.65	124.25	0.75	25
			System Methylcyclohexane-Toluene			
$\tilde{G}^E$	333.15**	859.68	-50.34	0.00	2.05	40
$\tilde{G}^E$	353.15	800.95	-52.45	0.00	1.36	40
$\tilde{G}^E$	363.15	772.13	-34.59	0.00	1.90	40
$\tilde{G}^E$	373.15	733.27	-42.53	0.00	2.04	40
$\tilde{H}^E$	283.15**	2113.72	-98.31	0.00	3.75	44
$\tilde{H}^E$	298.15	2070.48	-90.23	0.00	10.52	44
			System n-Heptane-Methylcyclohexane			
$\tilde{G}^E$	304.65**	0.00	0.00	0.00		9
$\tilde{G}^E$	320.64	0.00	0.00	0.00		9
$\tilde{G}^E$	353.10	0.00	0.00	0.00		9
$\tilde{H}^E$	298.15**	136.33	-27.68	0.00	0.58	25
$\tilde{H}^E$	323.15	75.63	-17.78	0.00	0.08	25

* Standard deviation, defined by Equation (8)

** Integration constants

Excess volumes were determined using the equation

$$\tilde{V}^E = \tilde{V} - (x_1 \tilde{V}_1 + x_2 \tilde{V}_2) \quad (28)$$

The excess volume data were fitted by a Redlich-Kister equation using the method of least squares:

$$\tilde{V}^E = x_1 x_2 [C_o + C_1 (x_1 - x_2)] \quad (29)$$

Experimental and smoothed excess volume data are given in Table 11, Appendix C, and Table 14, Appendix E, respectively. The equations representing the smoothed data are given in Table 13, Appendix E.

Figure 3 shows the excess volumes reported in this work together with data taken from the literature. Excess volumes of the system n-heptane-toluene were measured at 298.15 K by Tsao and Smith[46] and Mathieson and Thynne[26]. Since the results of this work were obtained at 293.15 K the data are not strictly comparable. However, the error introduced by the difference in temperature is believed to be small. The data of Tsao and Smith agree well with the results of this work, although they scatter considerably. Mathieson and Thynne report only two data points, which are about 60 per cent higher than the data reported in this work. The agreement with the six data points of Tsao and Smith is considered to be more significant than the disagreement with the two points of Mathieson and Thynne.

No excess volume measurements for the system methylcyclohexane-toluene were found in the literature.

The excess volume of the system n-heptane-methylcyclohexane has been measured by Brandt[8]. Although he reports a positive excess volume

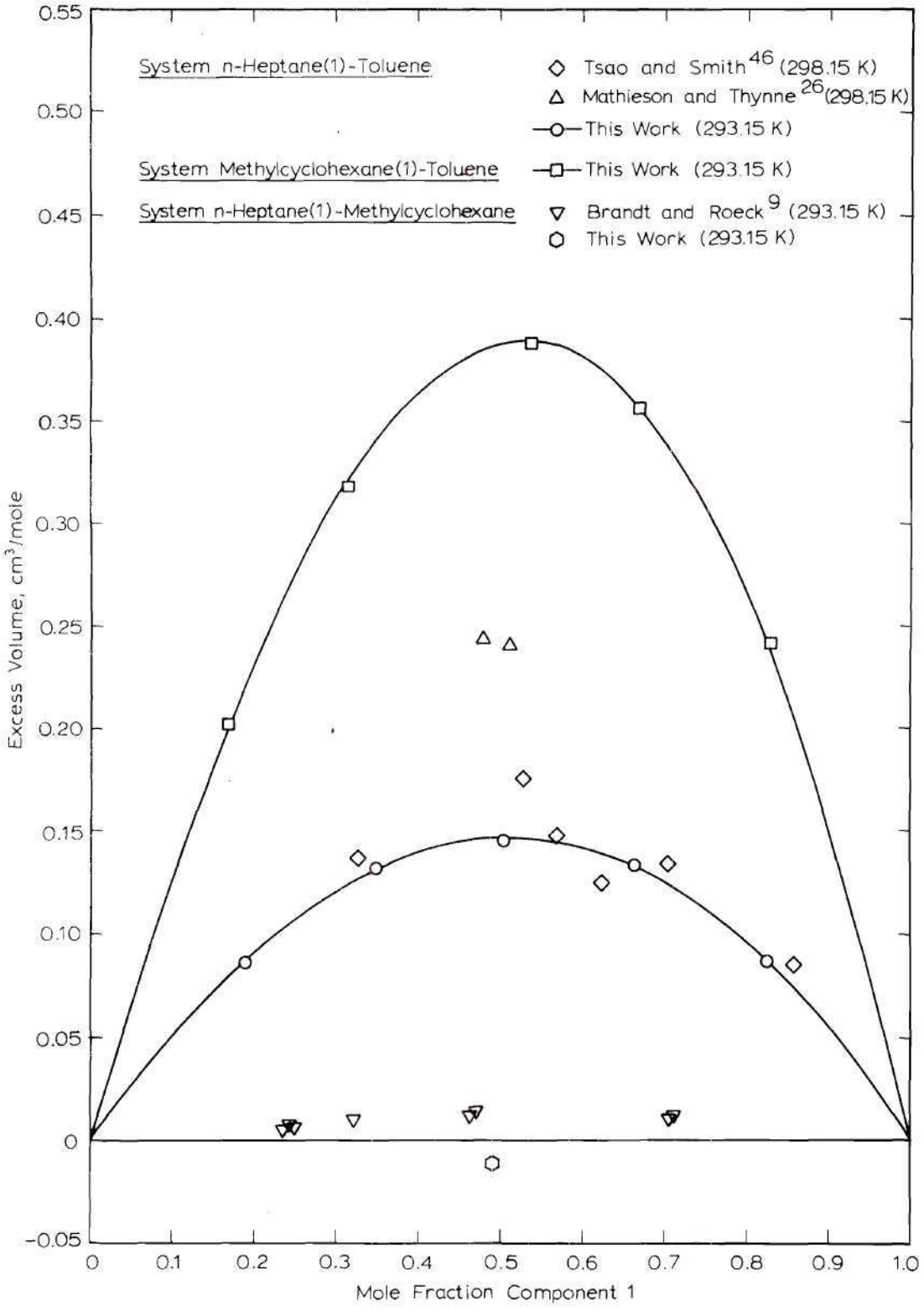


Figure 3. Excess Volumes

as opposed to a negative excess volume found in this work, the agreement is considered to be satisfactory since the absolute values are very small in both cases. The excess volume may probably be taken as zero for most practical purposes.

Results and Discussion

From the integration constants given in Table 6 and the equations for the excess heat capacity given in Table 13, Appendix E, the quantities $\tilde{H}^E$, $\tilde{G}^E$, $\tilde{S}^E$, and $\tilde{C}_p{}^E$ can be determined using Equations (19), (20), and (16). For the systems n-heptane-toluene and methylcyclohexane-toluene, the resulting equations are of the Redlich-Kister form, with temperature-dependent coefficients. For the system n-heptane-methylcyclohexane, the functions $\tilde{H}^E$, $\tilde{G}^E$, $\tilde{S}^E$, and $\tilde{C}_p{}^E$ were derived for the mixture composition used in the heat capacity measurements (48.910 mole per cent n-heptane), which may for all practical purposes be regarded as an equimolar mixture.

The equations representing the derived excess thermodynamic functions are listed in Table 13, Appendix E. The derived excess properties are tabulated in Table 14, Appendix E. For the systems n-heptane-toluene and methylcyclohexane-toluene, the activity coefficients γ_1 and γ_2 are also given.

For the systems n-heptane-toluene and methylcyclohexane-toluene, the excess free energy, enthalpy, entropy, and heat capacity are shown in Figures 4, 5, 6, and 7, respectively. The corresponding functions for the system n-heptane-methylcyclohexane are shown in Figure 8 for the equimolar mixture.

The excess heat capacities are considered to be accurate to

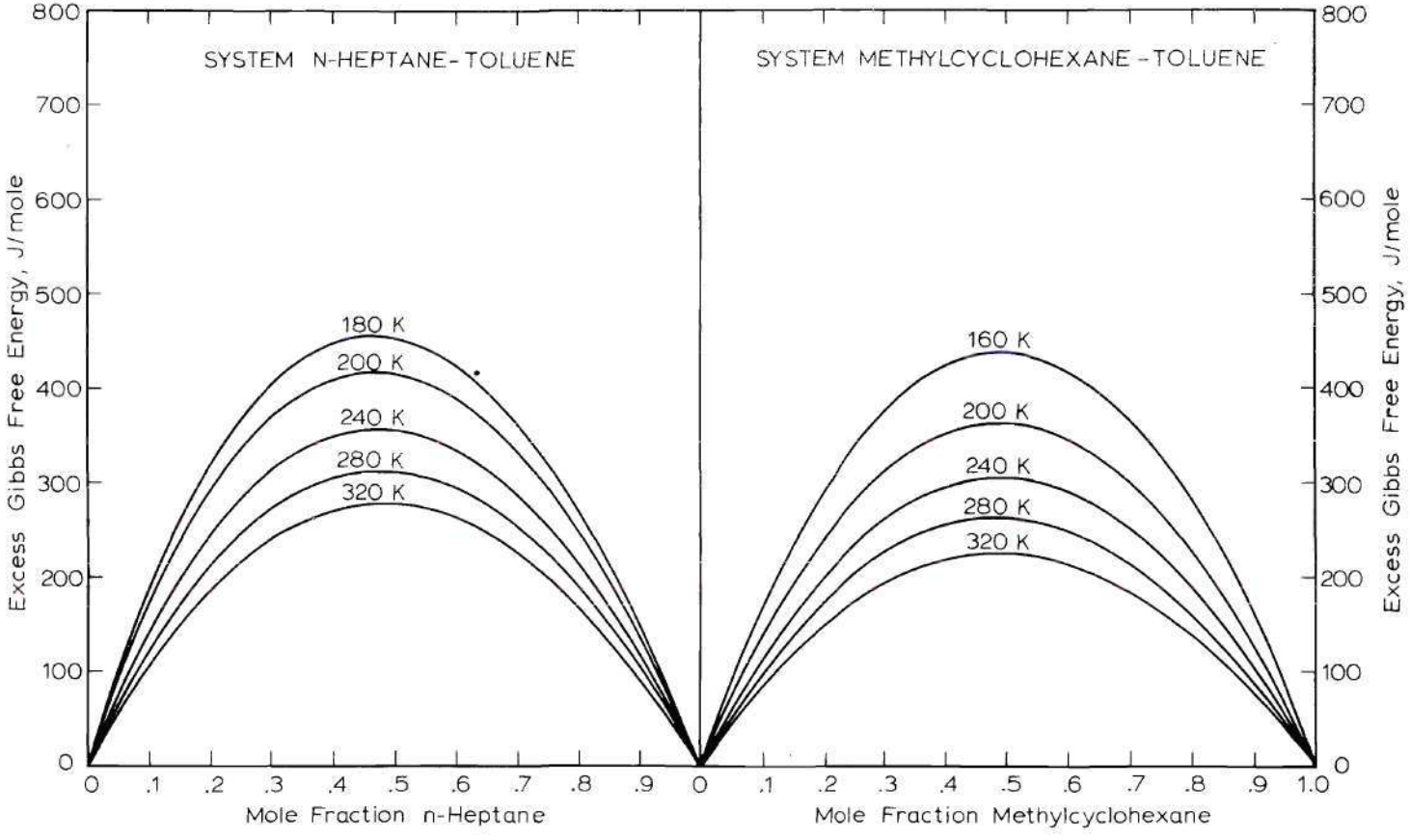


Figure 4. Excess Gibbs Free Energy of the Systems n-Heptane-Toluene and Methylcyclohexane-Toluene

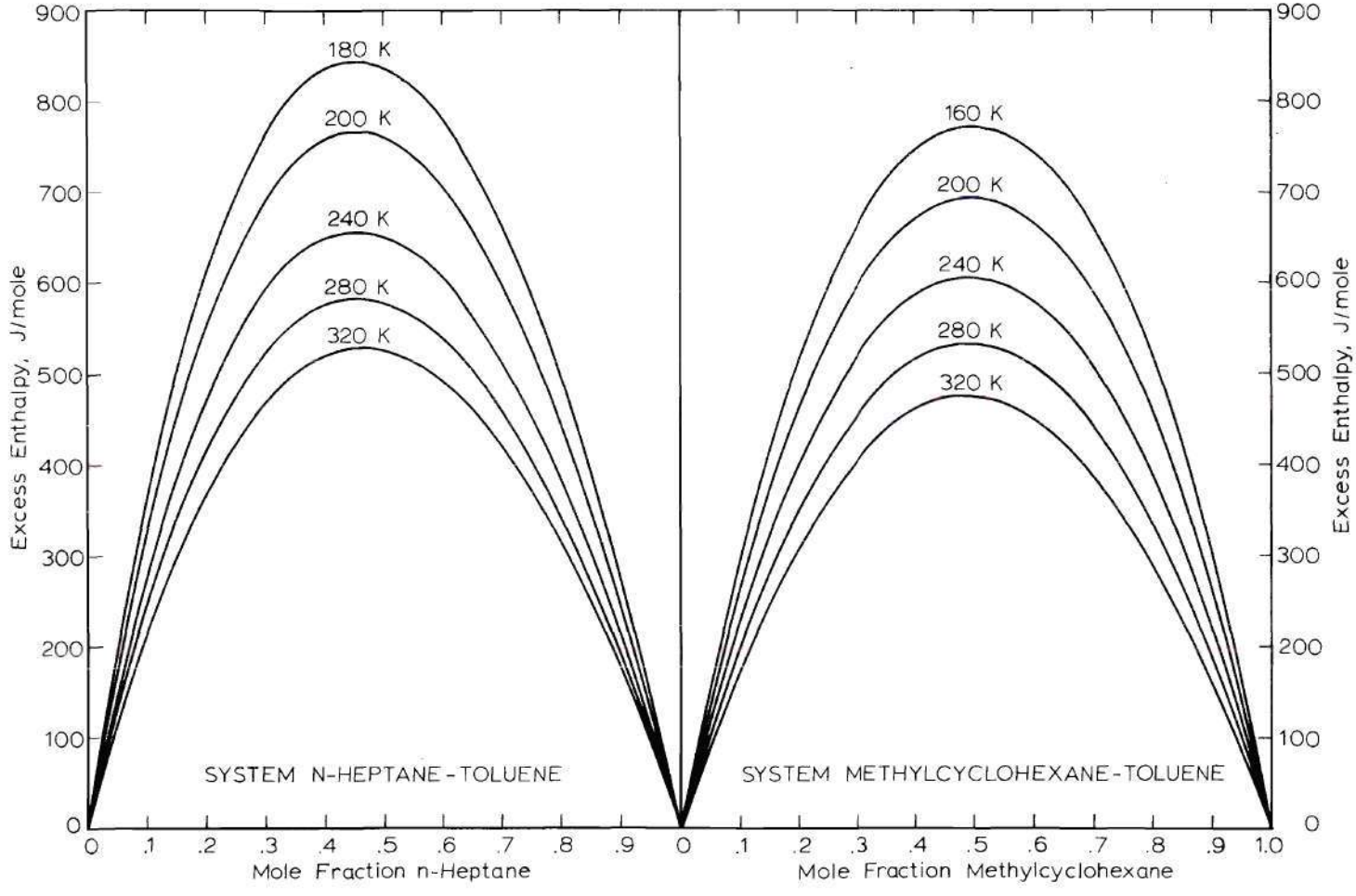


Figure 5. Excess Enthalpy of the Systems n-Heptane-Toluene and Methylcyclohexane-Toluene

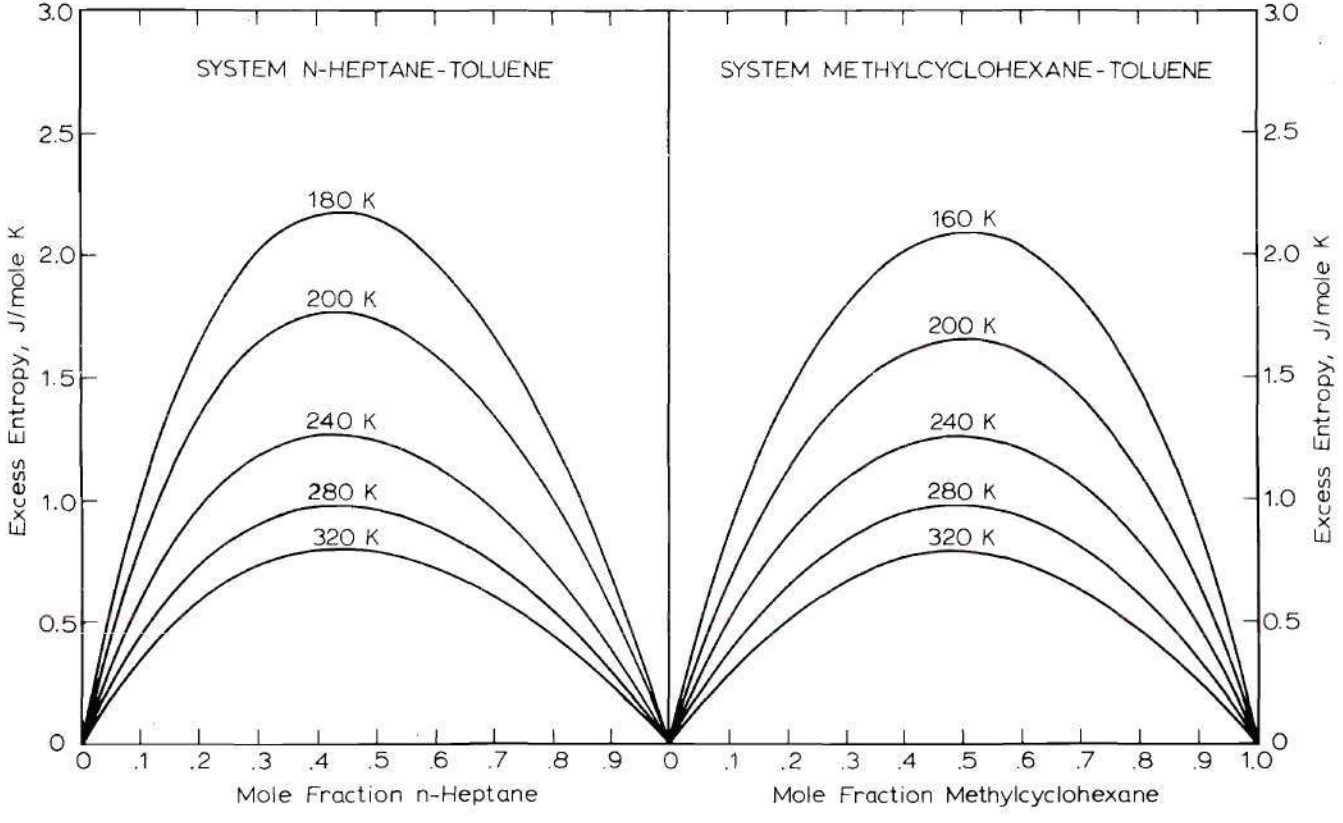


Figure 6. Excess Entropy of the Systems n-Heptane-Toluene and Methylcyclohexane-Toluene

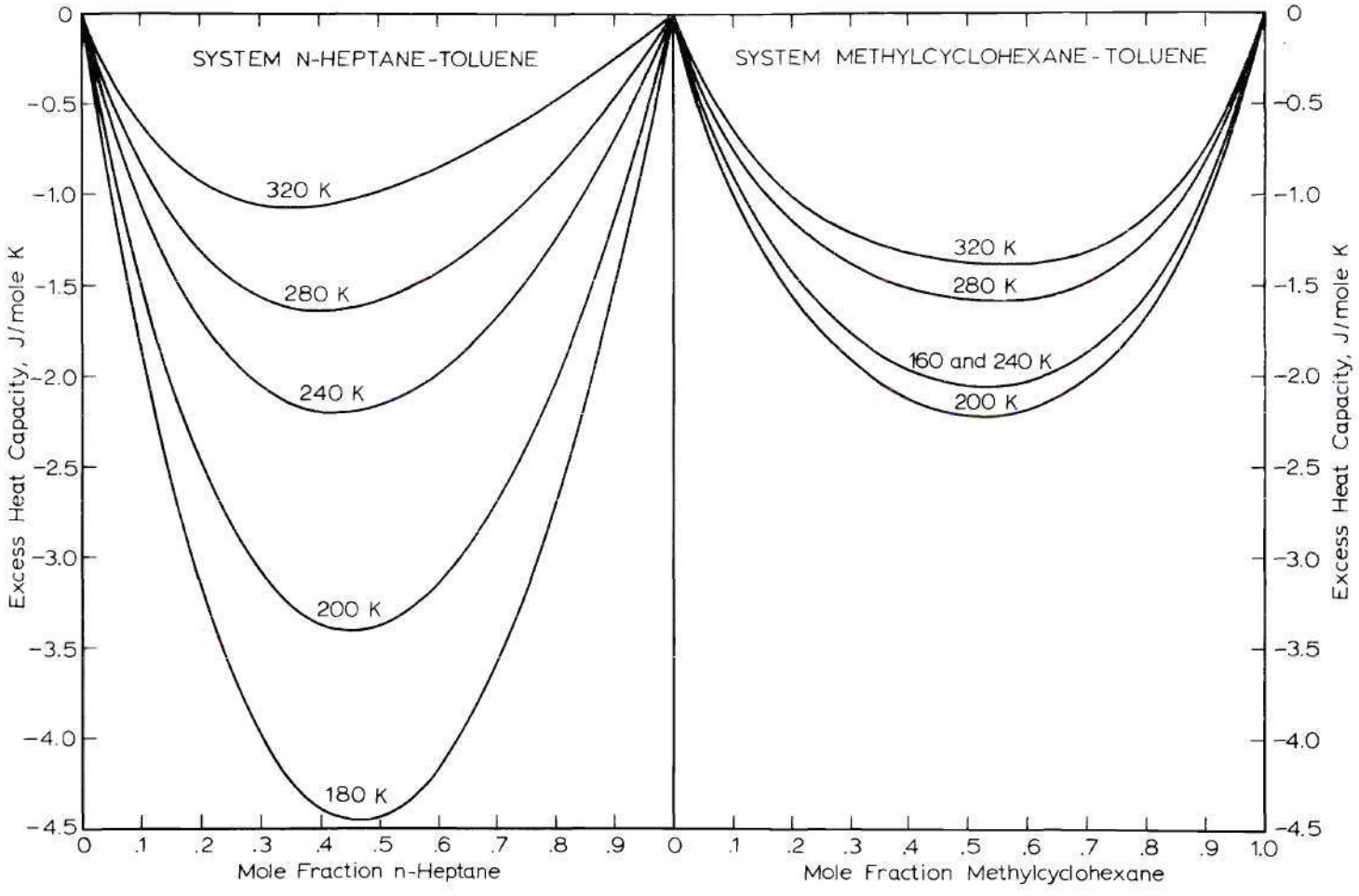


Figure 7. Excess Heat Capacity of the Systems n-Heptane-Toluene and Methylcyclohexane-Toluene

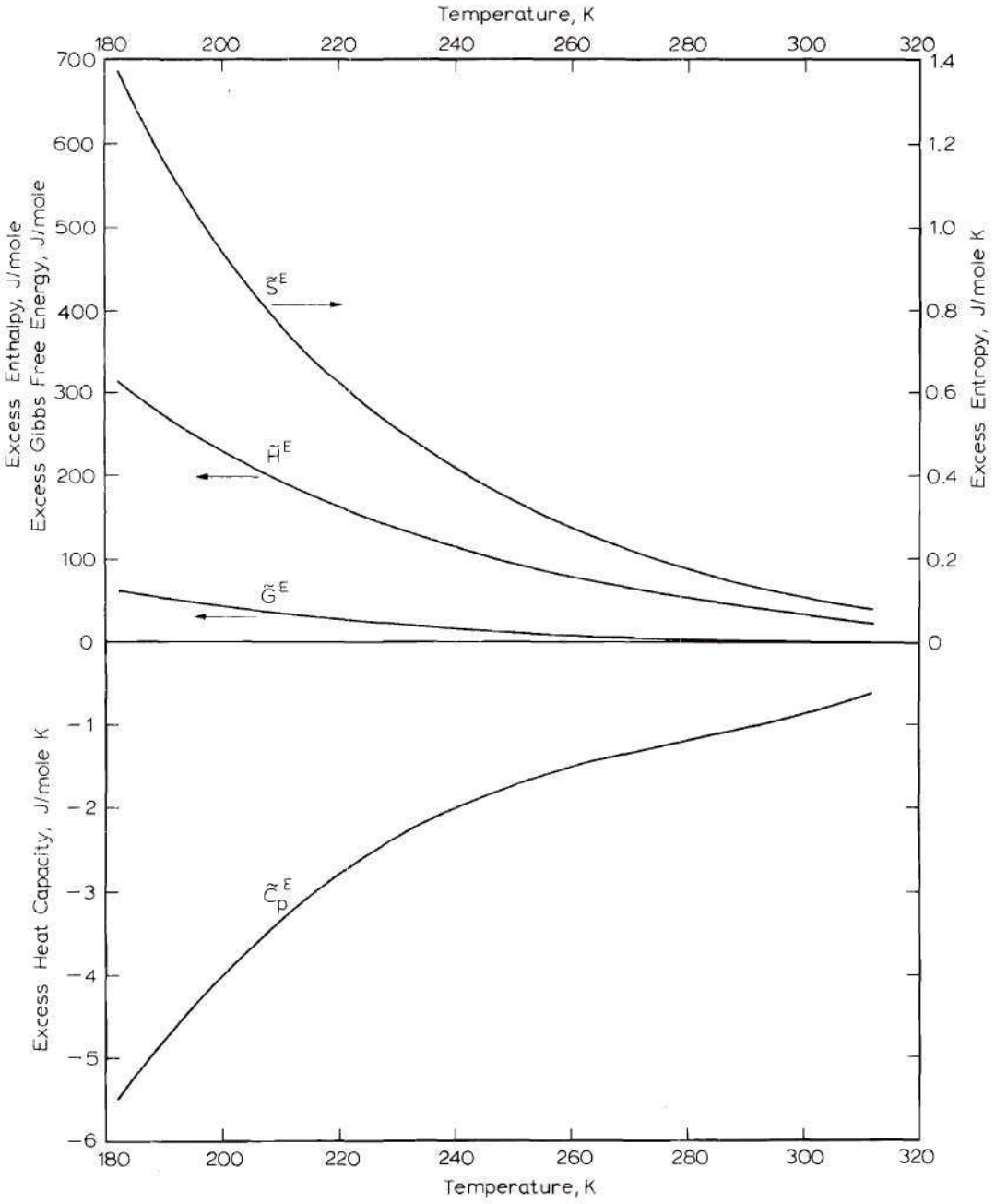


Figure 8. Excess Thermodynamic Functions of an Equimolar Mixture of n-Heptane and Methylcyclohexane

0.25 J/mole K. This seems to be a conservative estimate considering that the data could be fitted with a standard deviation of only 0.1 J/mole K. Since the derived $\tilde{H}^E$ values are as much as 120 K below the temperatures of the integration constants, a systematic error of 0.25 J/mole K would introduce an error of up to 30 J/mole K in the derived excess enthalpy. If the accuracy of the integration constants is assumed to be 20 J/mole, the error in the derived excess enthalpy should be no larger than 50 J/mole at the lowest temperature and decrease with increasing temperature to about 20 J/mole at room temperature.

The derived excess free energy is not very sensitive to errors in $\tilde{H}^E$. It can be shown that an error of the magnitude estimated above would change the value of $\tilde{G}^E$ at the lowest temperature by about 15 J/mole. If the accuracy of the integration constants is taken as 15 J/mole, the error in the derived excess free energy should be no larger than 25 J/mole at the lowest temperature and 15 J/mole at room temperature.

An analysis of the excess entropy data showed that the accuracy is about 0.24 J/mole K at the lowest temperatures and about 0.12 J/mole K at room temperature.

The excess volume measurements are believed to be accurate within 0.01 cm^3/mole, which corresponds to 6.8 per cent of the maximum value for the system n-heptane-toluene and to 2.6 per cent for the system methylcyclohexane-toluene.

The dependence of the excess thermodynamic properties on composition is very nearly quadratic for both systems, in accordance with the general

behavior of mixtures formed by non-polar molecules of similar size. The only exception is the excess heat capacity of the system n-heptane-toluene, which shows a marked asymmetry near room temperature. However, the values of the excess heat capacity are very small in this region, and the relative error is large. The shape of the curve will therefore depend on the type of fit chosen. The following discussion will be limited to the excess thermodynamic functions for equimolar mixtures.

The systems n-heptane-toluene and methylcyclohexane-toluene show a very similar temperature dependence of the excess free energy, enthalpy, and entropy. All these functions increase with decreasing temperature. The excess enthalpy of an equimolar mixture of n-heptane and toluene increases from about 530 J/mole at 320 K to 840 J/mole at 180 K. The excess enthalpy of methylcyclohexane-toluene increases from 480 J/mole at 320 K to 770 J/mole at 160 K. The excess free energy of the system n-heptane-toluene increases from about 280 J/mole at 320 K to 450 J/mole at 180 K. For the system methylcyclohexane-toluene, the corresponding values are 220 J/mole at 320 K and 440 J/mole at 160 K. These excess free energies are unusually high for hydrocarbon mixtures. If $\tilde{G}^E$ shows a quadratic dependence on composition, a mixture will separate into two phases when the ratio $\tilde{G}^E/RT$ reaches the value 0.5. This ratio is 0.30 for n-heptane-toluene at 180 K and 0.33 for methylcyclohexane-toluene at 160 K. Cloud point experiments with approximately equimolar mixtures showed no phase separation down to the freezing point for the two systems.

The excess entropy of an equimolar mixture of n-heptane and

toluene increases from about 0.8 J/mole K at 320 K to 2.1 J/mole K at 180 K. The excess entropy of the system methylcyclohexane-toluene increases from 0.8 J/mole K at 320 K to 2.1 J/mole K at 160 K.

The excess heat capacity curves of both systems are very similar above 240 K. Below this temperature, the excess heat capacity of the system n-heptane-toluene becomes rapidly more negative, whereas the excess heat capacity of the system methylcyclohexane-toluene levels off and even shows a slight increase below 200 K. However, this difference in the shapes of the $\tilde{C}_p^E$ curves has only a relatively small effect on the derived excess enthalpies and entropies. Below 240 K, the excess enthalpy and entropy of n-heptane-toluene increase faster with decreasing temperature than the corresponding functions for methylcyclohexane-toluene. This effect is discussed in Chapter VI.

The excess volumes of the two systems are quite different. With 0.39 cm^3/mole at 293.15 K, the excess volume of an equimolar mixture of methylcyclohexane and toluene is about 2.6 times as high as the excess volume of n-heptane-toluene (0.15 cm^3/mole).

Although the system n-heptane-methylcyclohexane shows nearly ideal behavior at room temperature, it becomes rather nonideal at low temperatures. The excess enthalpy of the equimolar mixture increases from about 20 J/mole at 320 K to 320 J/mole at 180 K. The excess entropy increases from about 0.1 J/mole K at 320 K to 1.4 J/mole K at 180 K. The excess heat capacity decreases from -0.4 J/mole K at 320 K to -5.7 J/mole K at 180 K. These quantities show the strongest temperature dependence in the lowest third of the temperature range. Since the enthalpy and entropy effects nearly cancel each other, $\tilde{G}^E$ remains

relatively small. It increases from near zero at 320 K to about 60 J/mole at 180 K. The excess volume is near zero at 293.15 K.

CHAPTER VI

THEORETICAL CORRELATION OF THE DERIVED EXCESS THERMODYNAMIC PROPERTIES

Introduction

Three theoretical models are used to correlate the derived excess thermodynamic properties for the systems n-heptane-toluene and methylcyclohexane-toluene: the conformal solution theory, by Longuet-Higgins[24]; a modification of this theory allowing for the presence of orientation-dependent intermolecular forces, by Rowlinson and Sutton[37]; and a theory based on a cell model for liquid mixtures, by Flory[15].

Correlations Using the Conformal Solution Theory

The theory of conformal solutions was developed by Longuet-Higgins[24]. Derivations of the formulas can be found in the original paper and in books by Hill[17] and Prigogine (Reference 30, Chapter IV) and will not be presented here. However, the assumptions made in the theory will be briefly discussed:

1. The potential, u_{ij}, of a pair of molecules i and j conforms to a universal function,

$$u_{ij} = \epsilon_{ij}\, u(r_{ij}/\sigma_{ij}) \tag{30}$$

where r_{ij} denotes the distance between the centers of the molecules. ϵ_{ij} and σ_{ij} are scale factors having dimensions of energy and length, respectively.

2. Only pair interactions will be considered.

3. All molecular pairs involved have nearly the same parameters ϵ_{ij} and σ_{ij}, respectively.

4. Internal rotations and vibrations are not affected by intermolecular forces.

5. Classical statistical mechanics may be used, except for internal vibrations and rotations.

Assumption 1 is probably the most severe restriction on the generality of the treatment, since it implies that the molecules are spherically symmetric and obey the theorem of corresponding states[29]. However, the molecules dealt with in this work, especially n-heptane, are definitely non-spherical, and cannot be expected to obey the theorem of corresponding states accurately.

Assumption 2 is probably very good and is usually made in theories of liquid mixtures (see, e.g., Reference 35, Chapter VII).

Assumption 3 restricts the theory to molecules with similar size and energy parameters. Considering that all three components are C_7 hydrocarbons, this assumption seems reasonable.

Assumption 4 is not strictly valid. For instance, Scott et al.[41] note that the lower vibrational frequencies for toluene are not exactly the same in the liquid as in the gas. However, these effects are likely to be small.

Assumption 5 is probably excellent for the temperature range of this investigation.

The conformal solution theory expresses the excess thermodynamic functions of a mixture in terms of the configurational energy, $\tilde{U}_o$, and

the volume, $\tilde{V}_o$, of a reference species. Since the reference species is subject to the same assumptions as the components of the mixture, one of these components is usually chosen for this purpose. Toluene is used as reference species because it is the common component of both systems. $\tilde{U}_o$ and $\tilde{V}_o$ are derived in Appendix F.

If the quantities

$$e_{12} = (2\epsilon_{12} - \epsilon_{11} - \epsilon_{22})/\epsilon_{oo} \tag{31}$$

$$s_{12} = (2\sigma_{12} - \sigma_{11} - \sigma_{22})/\sigma_{oo} \tag{32}$$

are introduced, where the index o refers to the reference species and 1 and 2 to the components of the mixture, the conformal solution theory yields the following expressions for the excess thermodynamic properties:

$$\tilde{G}^E = x_1 x_2 [e_{12}\tilde{U}_o - 3s_{12}RT] \tag{33}$$

$$\tilde{H}^E = x_1 x_2 [e_{12}(\tilde{U}_o - T(\frac{\partial \tilde{U}_o}{\partial T})_P)] \tag{34}$$

$$\tilde{S}^E = x_1 x_2 [-e_{12}(\frac{\partial \tilde{U}_o}{\partial T})_P + 3s_{12}R] \tag{35}$$

$$\tilde{V}^E = x_1 x_2 [-e_{12}T(\frac{\partial \tilde{V}_o}{\partial T})_P + 3s_{12}\tilde{V}_o] \tag{36}$$

The theory predicts a quadratic dependence on the mole fraction for all excess thermodynamic properties. The experimental results show that this is very nearly the case for the two systems considered here (see Chapter V). It is therefore sufficient to examine the excess thermodynamic functions of the equimolar mixtures.

Equations (33) through (36) for the excess thermodynamic

functions contain two adjustable parameters, e_{12} and s_{12}. In principle, these parameters could be determined to give a best fit of any of the excess properties over the whole range of temperature. In practice, however, it is preferable to fit $\tilde{G}^E$ since $\tilde{H}^E$ and $\tilde{S}^E$ can be directly obtained from $\tilde{G}^E$ by differentiation, according to Equations (14) and (17). This means that if a good fit of the $\tilde{G}^E$ data is obtained, the derivatives, $\tilde{H}^E$ and $\tilde{S}^E$, will also be fitted reasonably well. However, a good fit of either $\tilde{H}^E$ or $\tilde{S}^E$ does not guarantee a good fit of $\tilde{G}^E$ because it is obtained from either of the former by integration, and thus also depends on an integration constant.

The parameter e_{12} was determined by fitting the theoretical excess free energy, $\tilde{G}^E_{th}$, as given by Equation (33), to the experimental excess free energy, $\tilde{G}^E_{exp}$, for the equimolar mixture over the temperature range of the experimental data. $\tilde{G}^E_{exp}$ is taken from Table 13, Appendix E. A least-squares method was used which consisted in minimizing the integral over the squares of the residuals,

$$I = \int_{T_1}^{T_2} (\tilde{G}^E_{exp} - \tilde{G}^E_{th})^2 dT \qquad (37)$$

T_1 and T_2 are the lowest and highest temperatures of the $\tilde{C}_p$ measurements, respectively. The minimum of I could be found analytically, but it is less cumbersome to evaluate the integral numerically for several trial values of e_{12} by using Simpson's rule and to determine the minimum by an iterative procedure. The other thermodynamic functions can then be computed using Equations (34), (35), and (36).

The influence of the parameter s_{12} on $\tilde{G}^E$, $\tilde{H}^E$, and $\tilde{S}^E$ is very

small. However, s_{12} has a large effect on $\tilde{V}^E$ since it is, by definition, closely related to the intermolecular distances. Two types of fits were therefore attempted:

1. If a fit of the excess volume is not desired, the parameter s_{12} can be set equal to zero, for the sake of simplicity. The best fit is then found by adjusting e_{12} such that I becomes a minimum.

2. If the excess volume is to be fitted, as well as the excess free energy, both parameters are used. The experimental excess volume of the equimolar mixture at 293.15 K is inserted into Equation (36), giving one relation between e_{12} and s_{12}. This relation is used to eliminate one of the parameters from Equation (33) for the excess free energy. The other parameter is then adjusted by minimizing I.

For both methods, the parameters used and the predicted excess thermodynamic functions are listed in Table 15, Appendix G. The predicted excess free energies, enthalpies, and entropies as functions of temperature are shown in Figures 9, 10, and 11.

It is apparent that it makes very little difference in the predicted values of $\tilde{G}^E$, $\tilde{H}^E$, and $\tilde{S}^E$, whether the volume parameter s_{12} is included or not. However, it is impossible to predict the excess volume from the energy data using the parameter e_{12}. The predicted excess volume for n-heptane-toluene is larger than that for methylcyclohexane-toluene, in disagreement with the experimental findings.

For both systems, the predicted temperature dependence of $\tilde{G}^E$ is too small. The discrepancy between theory and experiment becomes much more obvious for $\tilde{H}^E$ and $\tilde{S}^E$, which are obtained from $\tilde{G}^E$ by

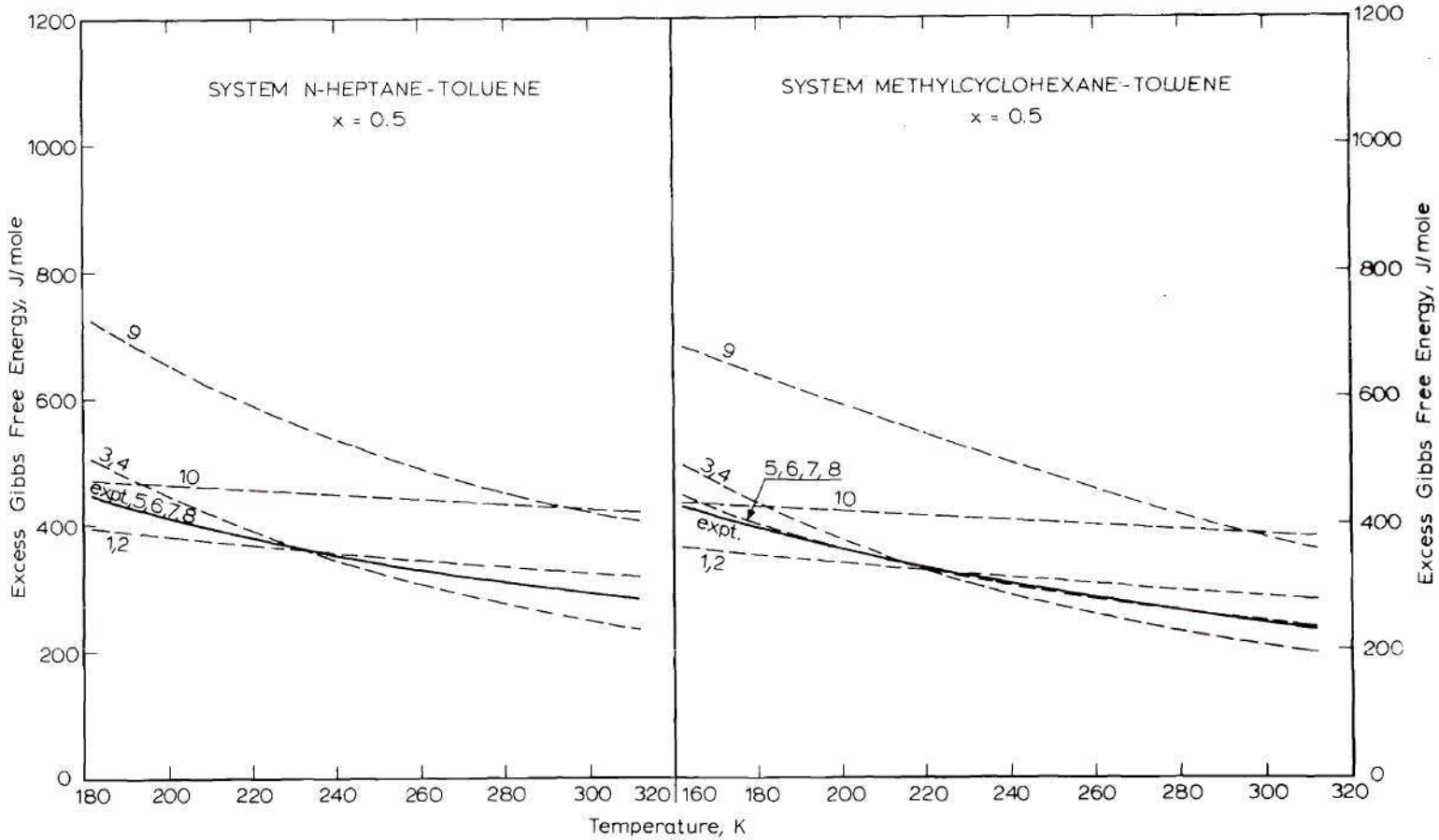


Figure 9. Predicted Excess Free Energy of the Systems n-Heptane-Toluene and Methylcyclohexane-Toluene (Numbers refer to methods of calculation given in Chapter VI and in Table 15, Appendix G)

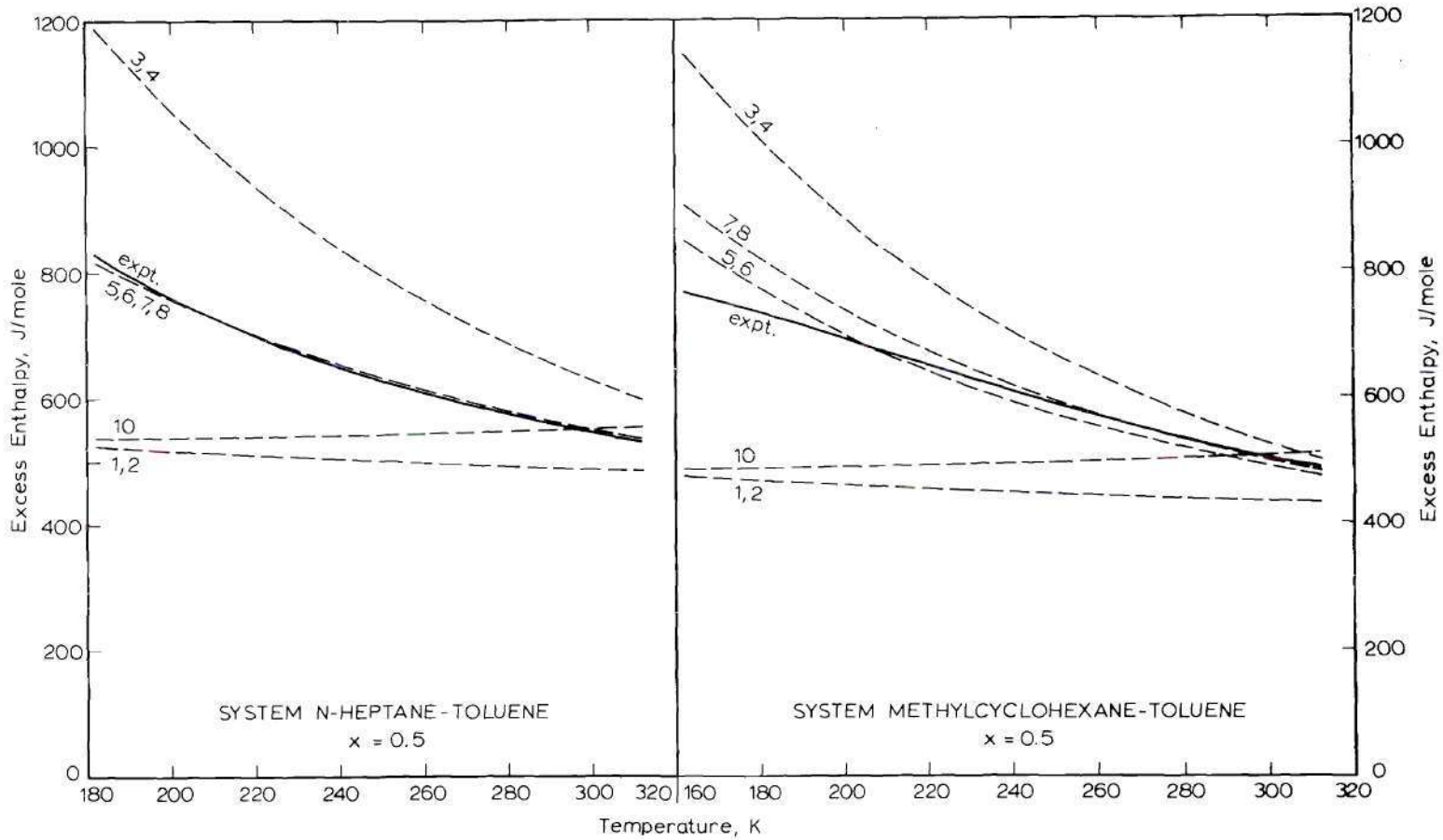


Figure 10. Predicted Excess Enthalpy of the Systems n-Heptane-Toluene and Methylcyclohexane-Toluene (Numbers refer to methods of calculation given in Chapter VI and in Table 15, Appendix G)

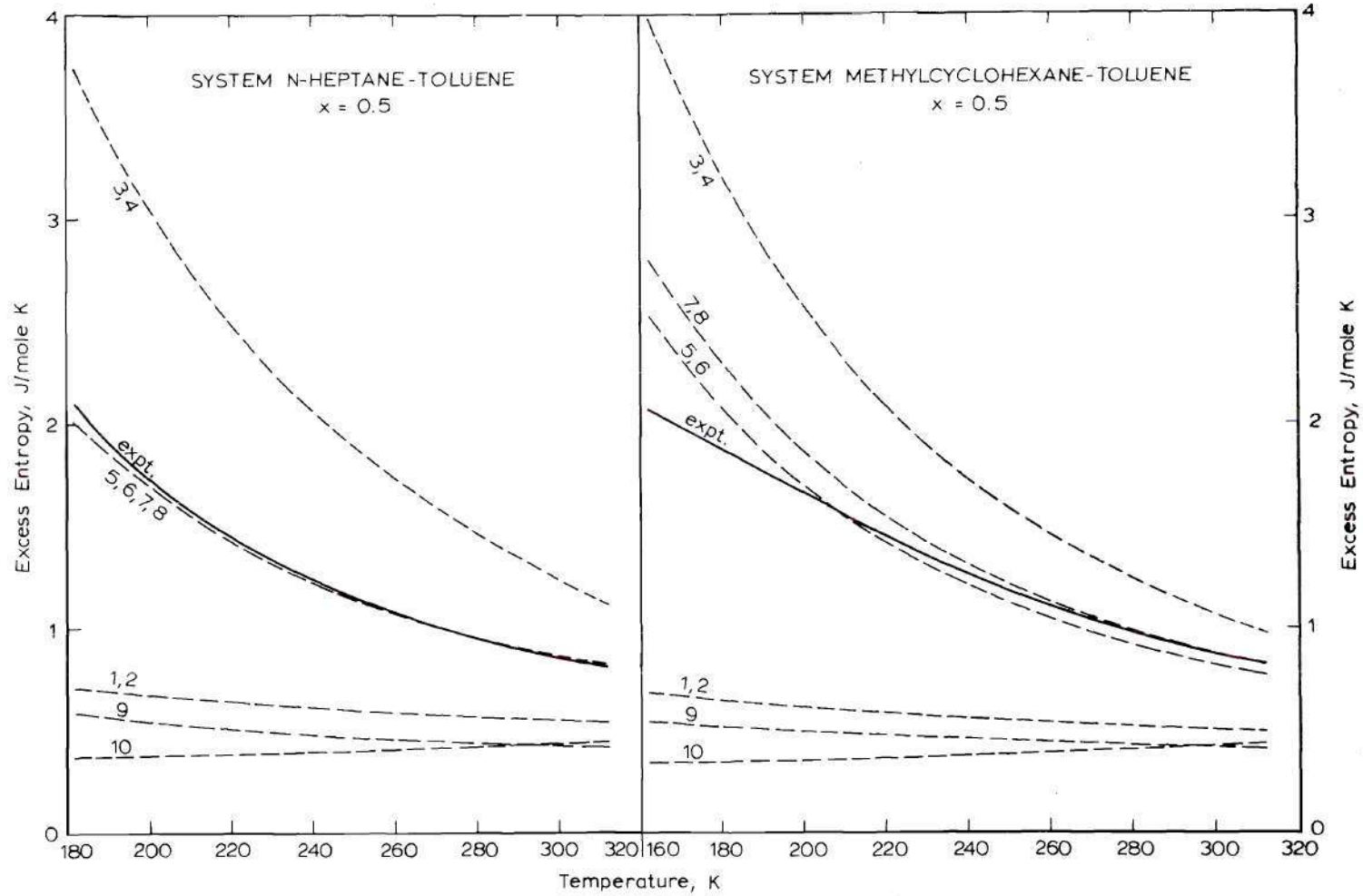


Figure 11. Predicted Excess Entropy of the Systems n-Heptane-Toluene and Methylcyclohexane-Toluene (Numbers refer to methods of calculation given in Chapter VI and in Table 15, Appendix G)

differentiation and therefore very sensitive to any deviations. Not only is the quantitative agreement poor, but the temperature dependence is qualitatively not well represented.

This result indicates that at least one of the assumptions made in the derivation of the conformal solution theory is unsatisfactory for this type of systems. This is most likely the assumption that the molecules are spherically symmetric, which is obviously not realistic.

Correlations Assuming Directional Intermolecular Forces

The assumption that orientation-dependent intermolecular forces are present in the systems investigated here is based on calculations of the lattice energy of crystalline benzene, by Banerjee and Salem[6], and Rae and Mason[32]. These authors show that the attractive forces between benzene molecules vary strongly with orientation, due to the highly anisotropic polarizability of the π-electron systems. Banerjee and Salem also show that the dispersive interactions between π-electrons are unusually strong. The π-electrons contribute 40 per cent of the lattice energy of benzene, although they represent only 20 per cent of all valence electrons.

Although the structure of liquid benzene is certainly much less ordered than that of the solid, the molecules will still have some tendency to favor orientations for which the attractive energy is large. This effect will decrease with increasing temperature, since the thermal motion of the molecules counteracts any order in the liquid.

When benzene is mixed with another liquid which shows no orientation effects, some of the strong π-π interactions between neighboring benzene molecules are broken, resulting in a positive

excess enthalpy. This effect will be larger at lower temperatures, where the benzene molecules are statistically more likely to assume orientations with large attractive energies.

Since the orientational forces in the mixture are weaker than in pure benzene, increased randomness of orientation results, which causes a positive excess entropy.

These effects have been found in mixtures of benzene with aliphatic or alicyclic hydrocarbons (see Chapter I). Mixtures containing toluene instead of benzene show the same effects, although the excess thermodynamic properties are smaller than for corresponding benzene mixtures (see Reference 35, Chapter IV). This can readily be explained by the more aliphatic character of toluene (16.7 per cent of the valence electrons are π-electrons vs. 20 per cent in benzene) and by the larger intermolecular distances (due to the larger molar volume), which weaken the π-π interactions.

Rowlinson and Sutton[37] have modified the conformal solution theory to allow for the presence of directional attractive forces. The repulsive part of the potential is still assumed to be spherical. The latter assumption is not very satisfactory because the repulsive potential is determined essentially by the shape of the molecule, and the molecules considered in this work are non-spherical. However, it is known that mixtures of saturated hydrocarbons differ only relatively little from ideality, even if their shapes are very different, such as in the systems n-hexane-cyclohexane, n-heptane-methylcyclohexane, or n-octane-tetraethylmethane (see Reference 35, Chapter IV). Most of the nonideality exhibited by mixtures of saturated and aromatic

hydrocarbons is therefore likely to be due to the effect of the attractive forces.

In the treatment of Rowlinson and Sutton, the first assumption made in the previous section is replaced by:

1 a. The potential of a pair of molecules, i and j, is given by

$$u_{ij}(r_{ij},\omega_{ij}) = 4\,\epsilon_{ij}\left[\left(\frac{\sigma_{ij}}{r_{ij}}\right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}}\right)^{6}\,(1 + a_{ij}g_{ij}(\omega_{ij}))\right] \qquad (38)$$

where ω_{ij} denotes all coordinates describing the mutual orientation of the molecules, a_{ij} is a constant, and g_{ij} is defined such that

$$\int g_{ij}\,d\omega_{ij} = 0 \qquad (39)$$

with the integration taken over all mutual orientations.

Equation (39) does not restrict the generality of the treatment, for the attractive potential can always be split up into a central and a non-central part in such a way as to satisfy Equation (39).

Although the unweighted average of the non-central potential over all orientations is zero, this does not mean it has no effect on the thermodynamic functions. Actually, mutual orientations with a large attractive energy are statistically favored over orientations with a small attractive energy. The effective energy to be inserted into the partition function is a statistical average of the form

$$u^{*}_{ij}(r_{ij},T) = -kT\,\ln\left[\int \exp(-u_{ij}/kT)\,d\omega_{ij} \Big/ \int d\omega_{ij}\right] \qquad (40)$$

Expanding the exponential up to the first non-vanishing term involving the non-central potential, Equation (40) becomes:

$$u^*_{ij}(r_{ij}, T) = 4\,\epsilon_{ij}\left[\left(\frac{\sigma_{ij}}{r_{ij}}\right)^{12}(1 - 2\,\delta_{ij}) - \left(\frac{\sigma_{ij}}{r_{ij}}\right)^{6}\right] \tag{41}$$

where the parameter δ_{ij} is defined as

$$\delta_{ij} = (a_{ij}^{\,2}\,\epsilon_{ij}/kT)\left(\int g_{ij}^{\,2} d\omega_{ij} / \int d\omega_{ij}\right) \tag{42}$$

By definition, δ_{ij} is inversely proportional to the temperature.

Rowlinson and Sutton define a parameter Δ_{12}, analogous to the parameters e_{12} and d_{12} used in the conformal solution theory:

$$\Delta_{12} = 2\,\delta_{12} - \delta_{11} - \delta_{22} \tag{43}$$

Like δ_{ij}, Δ_{12} is inversely proportional to the temperature and thus inconvenient to handle. For convenience, a parameter d_{12} will be used here, which is defined as

$$d_{12} = \Delta_{12}\,T \tag{44}$$

The parameter d_{12} is a constant, but unlike e_{12} and s_{12}, it has the dimension of temperature.

Extending the results of the conformal solution theory (see Equations (33) through (36)), the following relations for the excess thermodynamic functions are obtained[37]:

$$\tilde{G}^E = x_1 x_2\left[e_{12}\tilde{U}_o - 3s_{12}RT + d_{12}(2\tilde{U}_o/T + R)\right] \tag{45}$$

$$\tilde{H}^E = x_1 x_2\left[e_{12}\left(\tilde{U}_o - T\left(\frac{\partial \tilde{U}_o}{\partial T}\right)\right) + d_{12}\left(\frac{4\tilde{U}_o}{T} - 2\left(\frac{\partial \tilde{U}_o}{\partial T}\right)_P + R\right)\right] \tag{46}$$

$$\tilde{S}^E = x_1 x_2\left[-e_{12}\left(\frac{\partial \tilde{U}_o}{\partial T}\right)_P + s_{12}(3R) + d_{12}\left(\frac{2\tilde{U}_o}{T^2} - \frac{2}{T}\left(\frac{\partial \tilde{U}_o}{\partial T}\right)_P\right)\right] \tag{47}$$

$$\tilde{V}^E = x_1 x_2 \left[-e_{12} T \left(\frac{\partial \tilde{V}_o}{\partial T}\right)_P + s_{12}(3\tilde{V}_o) + d_{12}\left(-\frac{\tilde{V}_o}{T} - 2\left(\frac{\partial \tilde{V}_o}{\partial T}\right)_P\right)\right] \qquad (48)$$

In order to test the ability of this theory to represent the excess thermodynamic functions of the systems n-heptane-toluene and methylcyclohexane-toluene, the following fits were attempted, using Equation (37):

3.* To illustrate the effect of the parameter d_{12}, the other two parameters are set equal to zero. d_{12} is then adjusted to give a best fit of the experimental excess free energy over the whole temperature range, using the method described in the preceding section.

4. The parameters d_{12} and s_{12} are used, e_{12} being set equal to zero. They are determined by fitting the excess volume at 293.15 K exactly and by least-square fitting the excess free energy as a function of temperature.

5. The parameters e_{12} and d_{12} are used, s_{12} being set equal to zero. This corresponds to the case where the influence of both central and non-central forces is important, and where a fit of the excess volume data is not necessary. The excess free energy is fitted over the whole temperature range by adjusting the parameters e_{12} and d_{12}.

6. The parameters e_{12}, d_{12}, and s_{12} are used. They are determined by fitting the excess volume at 293.15 K exactly and by fitting the excess free energy as a function of temperature.

The results of the calculations are shown in Figures 9, 10, and 11, and in Table 15, Appendix G.

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* The numbers 1 and 2 are assigned to methods described in the preceding section.

As in the conformal solution theory, the volume parameter s_{12} has no significant influence on the fit of the $\tilde{H}^E$, $\tilde{G}^E$, and $\tilde{S}^E$ data.

If the nonideality is attributed to the effect of the non-central forces alone (Methods 3 and 4) the predicted variation of $\tilde{G}^E$ with temperature is too large. The predicted $\tilde{H}^E$ and $\tilde{S}^E$ values are much too large and show a much greater temperature dependence than the experimental values. These results are exactly the opposite to the results of the conformal solution theory (Methods 1 and 2), which attributes the observed non-ideality to the effect of the central forces alone.

If both e_{12} and d_{12} are treated as adjustable parameters, $\tilde{G}^E$ of both systems can be fitted well within the experimental accuracy over the temperature range covered in this work. The $\tilde{H}^E$ and $\tilde{S}^E$ values predicted by the theory also fit the experimental values extremely well in the case of n-heptane-toluene and reasonably well in the case of methylcyclohexane-toluene.

Table 16, Appendix G, shows the contributions of the various parameters to the excess functions, computed from Method 6. Again, the results are similar for both systems. The contribution of the directional forces (represented by d_{12}) to both $\tilde{H}^E$ and $\tilde{S}^E$ is greater than the contribution of the central forces (represented by e_{12}), especially at low temperatures. However, both terms contribute about equally to $\tilde{G}^E$. The contribution of the volume parameter s_{12} to $\tilde{S}^E$ and $\tilde{G}^E$ is only a few per cent, and it does not enter the expression for $\tilde{H}^E$ at all (see Equation (46)). The contributions of the three parameters to $\tilde{V}^E$ are of comparable magnitude. The theory predicts $\tilde{V}^E$

to be almost constant over the whole temperature range. No experimental data are available to verify this prediction. Measurements on the related system benzene-cyclohexane show that the excess volume is independent of temperature over the range from 293.15 to 343.15 K (see Reference 35, Chapter IV), which gives some support to the theoretical predictions.

The success of the theory of Rowlinson and Sutton in correlating the excess thermodynamic properties of n-heptane-toluene and methylcyclohexane-toluene suggests that the temperature dependence of these properties may be predictable from a knowledge of their values at room temperature alone. Two methods of prediction were attempted:

7. The experimental values of $\tilde{G}^E$ and $\tilde{H}^E$ at 293.15 K were inserted into Equations (45) and (46), respectively. The parameters e_{12} and d_{12} were determined from these two equations. The parameter s_{12} was assumed to be zero.

8. The experimental values of $\tilde{G}^E$, $\tilde{H}^E$, and $\tilde{V}^E$ at 293.15 K were inserted into Equations (45), (46), and (48), respectively. The parameters e_{12}, d_{12}, and s_{12} were determined from these equations.

The excess thermodynamic functions computed from these two methods are shown in Figures 9, 10, and 11, and in Table 15, Appendix G. As in the previous fits, the predicted values of $\tilde{G}^E$, $\tilde{H}^E$, and $\tilde{S}^E$ are not significantly affected by the parameter s_{12}.

For the system n-heptane-toluene, the predicted excess free energy, enthalpy, and entropy agree with the experimental data well within the accuracy of measurement, down to the lowest temperatures. For the system methylcyclohexane-toluene, the agreement is not quite

as good, but still very satisfactory considering that the prediction covers a range of more than 130 degrees, from 293.15 K down to 162 K.

It would be interesting to see whether these methods are also able to predict the temperature dependence of the excess thermodynamic properties in the region above room temperature. Unfortunately, such a test is only possible for the excess free energy of the system methylcyclohexane-toluene, which has been measured by Schneider[40] up to 373.15 K, which is 80 degrees above the reference temperature of 293.15 K. Table 15, Appendix G, shows that the agreement between the predicted and the experimental values is excellent.

Correlations Using the Theory of Flory

Description of the Theory

Flory[15] has proposed a theory for mixtures of non-spherical molecules which is more empirical than the theories presented in the preceding sections. Only a brief discussion will be given here; the original paper should be consulted for details. Flory's notation will be followed here although it is not always consistent with the notation used in the remainder of this work.

Flory assumes that the forces between polyatomic molecules effectively arise from the surfaces of adjoining molecules. Each molecule is divided into r segments, each of which has s contact sites. The number of segments per molecule is proportional to the volume of the molecule. The total number of contact sites per molecule, rs, is proportional to the surface area of the molecule. The mean intermolecular energy of the liquid, E_o, is assumed to be inversely proportional to the volume per segment,

$$E_o = -Nrs\eta/2\upsilon \tag{49}$$

where N is the number of molecules, υ is the volume of a segment, and η is a constant characterizing the energy of interaction for a pair of neighboring sites. Starting from these assumptions, Flory derives a reduced equation of state:

$$\tilde{p}\tilde{v}/\tilde{T} = \tilde{v}^{1/3}/(\tilde{v}^{1/3} - 1) - 1/\tilde{v}\tilde{T} \tag{50}$$

The reduced quantities $\tilde{v}$, $\tilde{T}$, and $\tilde{p}$ are defined as

$$\tilde{v} = v/v^* \tag{51}$$

$$\tilde{p} = p/p^* \tag{52}$$

$$\tilde{T} = T/T^* \tag{53}$$

v denotes the molar volume, and v*, p*, and T* are characteristic quantities for each liquid.

The theory is extended to a binary mixture by introducing a parameter X_{12} which characterizes the difference in the energy of interaction between neighboring molecules of different species from the average of the interactions in the pure component liquids:

$$X_{12} = s_1(\eta_{11} + \eta_{22} - 2\eta_{12})/2\upsilon^{*2} \tag{54}$$

The quantity υ^* is defined as

$$\upsilon^* = \upsilon/\tilde{v} \tag{55}$$

and is the same for all species. Flory has shown that the reduced temperature of a binary mixture is given by the expression:

$$\tilde{T} = (\phi_1 p_1^* \tilde{T}_1 + \phi_2 p_2^* \tilde{T}_2)/(\phi_1 p_1^* + \phi_2 p_2^* - \phi_1 \theta_2 X_{12}) \tag{56}$$

where the segment fractions, ϕ_1 and ϕ_2, are defined as

$$\phi_2 = 1 - \phi_1 = x_2/(x_2 + x_1 r_1/r_2) \tag{57}$$

and the site fraction θ_2 by

$$\theta_2 = \phi_2/(\phi_2 + \phi_1 s_1/s_2) \tag{58}$$

The molar excess free energy, enthalpy, entropy, and volume are:

$$\tilde{G}^E = x_1 p_1^* v_1^* [\tilde{v}_1^{-1} - \tilde{v}^{-1} + 3\tilde{T}_1 \ln(\frac{\tilde{v}_1^{1/3} - 1}{\tilde{v}^{1/3} - 1})]$$

$$+ x_2 p_2^* v_2^* [\tilde{v}_2^{-1} - \tilde{v}^{-1} + 3T_2 \ln(\frac{\tilde{v}_2^{1/3} - 1}{\tilde{v}^{1/3} - 1})] + x_1 v_1^* \theta_2 X_{12} \tilde{v}^{-1} \tag{59}$$

$$\tilde{H}^E = x_1 p_1^* v_1^* (\tilde{v}_1^{-1} - \tilde{v}^{-1}) + x_2 p_2^* v_2^* (\tilde{v}_2^{-1} - \tilde{v}^{-1}) + x_1 v_1^* \theta_2 X_{12} \tilde{v}^{-1} \tag{60}$$

$$\tilde{S}^E = -3[\frac{x_1 p_1^* v_1^*}{T_1^*} \ln(\frac{\tilde{v}_1^{1/3} - 1}{\tilde{v}^{1/3} - 1}) + \frac{x_2 p_2^* v_2^*}{T_2^*} \ln(\frac{\tilde{v}_2^{1/3} - 1}{\tilde{v}^{1/3} - 1})] \tag{61}$$

$$\tilde{V}^E = (x_1 v_1^* + x_2 v_2^*)(\tilde{v} - \phi_1 \tilde{v}_1 - \phi_2 \tilde{v}_2) \tag{62}$$

Parameters for the Pure Components

At zero pressure, the reduced equation of state becomes

$$\tilde{T} = (\tilde{v}^{1/3} - 1)/\tilde{v}^{4/3} \tag{63}$$

Equation (63) is differentiated with respect to temperature and rearranged to give

$$\tilde{v} = [(1 + 4\alpha T/3)/(1 + \alpha T)]^3 \qquad (64)$$

Equation (64) permits the determination of $\tilde{v}$ if the coefficient of thermal expansion, α, is known at a certain temperature. If the molar volume, v, is known at the same temperature, the characteristic volume, v*, can be computed from Equation (51). Equation (63) serves to determine the corresponding value of $\tilde{T}$, which is inserted into Equation (53) to determine T*.

Differentiation of Equation (50) with respect to pressure yields for the limit of zero pressure:

$$p^* = T\tilde{v}^2\alpha/\beta \qquad (65)$$

This equation serves to determine the characteristic pressure, p*, from the isothermal compressibility, β.

Table 7 lists the parameters used for the pure components. All compressibilities were determined from isothermal measurements. The compressibility of n-heptane was measured by Eduljee et al.[14], and the compressibilities of methylcyclohexane and toluene were measured by Shinoda and Hildebrand[43]. Molar volumes and thermal expansion coefficients were computed from densities reported in the API Tables[2].

Determination of the Interaction Parameter

Abe and Flory[1] applied this theory to a wide variety of binary mixtures of non-polar molecules. They determined the interaction parameter X_{12} by fitting the experimental excess enthalpy and then computed the other excess functions from X_{12}. This procedure was adopted here.

Table 7. Parameters Used in the Theory of Flory (T = 298.15 K)

		n-Heptane	Methylcyclohexane	Toluene
α	K^{-1}	1.251×10^{-3}	1.137×10^{-3}	1.070×10^{-3}
β	cm^3/J	1.470×10^{-3}	1.203×10^{-3}	9.480×10^{-4}
v	cm^3/mole	147.47	128.34	106.86
p*	J/cm^3	426.78	458.30	536.13
v*	cm^3/mole	113.70	100.65	84.67
T*	K	4657.3	4884.8	5041.9

Since the number of segments, r, was chosen proportional to the volume of the molecules it follows that

$$r_1/r_2 = v_1^*/v_2^* \tag{66}$$

The number of contact sites, rs, was assumed to be proportional to the surfaces of the molecules. For spherical molecules, this leads to the relation

$$s_1/s_2 = (v_2^*/v_1^*)^{1/3} \tag{67}$$

Thus the quantities ϕ_1, ϕ_2, and θ_2 can be determined from Equations (57) and (58).

For non-spherical molecules, the ratio s_1/s_2 depends not only on the ratio v_2^*/v_1^*, but also on the shape of the molecules. However, Equation (67) is adopted here for simplicity. A change in the ratio s_1/s_2 would only affect the numerical value of X_{12} (which is treated

here as an adjustable parameter), but not the derived excess thermodynamic properties.

Equations (56), (60), and (63) contain three unknown quantities, X_{12}, $\tilde{v}$, and $\tilde{T}$. Equations (56) and (63) can be combined to give

$$X_{12} = - \frac{\phi_1 p_1^* \tilde{T}_1 + \phi_2 p_2^* \tilde{T}_2}{\phi_1 \theta_2 (\tilde{v}^{1/3} - 1)/\tilde{v}^{4/3}} + \frac{\phi_1 p_1^* + \phi_2 p_2^*}{\phi_1 \theta_2} \tag{68}$$

Equation (60) is rearranged to yield

$$X_{12} = \frac{\tilde{H}^E - x_1 p_1^* v_1^* (\tilde{v}_1^{-1} - \tilde{v}^{-1}) - x_2 p_2^* v_2^* (\tilde{v}_2^{-1} - \tilde{v}^{-1})}{x_1 v_1^* \theta_2 \tilde{v}^{-1}} \tag{69}$$

The reduced volume, $\tilde{v}$, is adjusted by trial and error to make the quantity X_{12} equal for both equations. As a first guess, $\tilde{v}$ was taken to be

$$\tilde{v} = \phi_1 \tilde{v}_1 + \phi_2 \tilde{v}_2 \tag{70}$$

which corresponds to a zero excess volume. The value of $\tilde{v}$ was then improved by iteration until it changed by less than 10^{-6} from one step to the next one. The quantities $\tilde{G}^E$, $\tilde{S}^E$, and $\tilde{V}^E$ could then be determined from $\tilde{v}$ using Equations (59), (61), and (62), respectively.

If the assumptions of Flory's theory were exact, X_{12} would have to be a constant over the whole range of composition and temperature. The calculations show that X_{12} is indeed very nearly independent of composition for both systems, but is strongly temperature-dependent. Table 17, Appendix G, lists X_{12} as a function of composition for

298.15 K and as a function of temperature for the equimolar mixture. Table 15, Appendix G, and Figure 11 (Method 9) show that the predicted excess entropy is much too low over the whole temperature range, which means that the predicted excess Gibbs free energy is too high (see Table 15, Appendix G, and Figure 9). Similar results were obtained by Abe and Flory[1] for the systems cyclohexane-benzene, n-hexane-benzene, and n-heptane-benzene, for which the predicted excess entropies are one third to one half of the experimental values. Although the theory of Flory is not restricted to spherical molecules, it does not take any orientation effects into account, which is the most likely reason for its failure to explain the observed excess entropy. However, the theory correctly predicts the excess volume of the system n-heptane-toluene to be smaller than that of the system methylcyclohexane-toluene, although the numerical agreement is poor for the former system (the predicted excess volume is 80 per cent higher than the experimental value for the system n-heptane-toluene and 9 per cent lower for the system methylcyclohexane-toluene).

Another way of testing Flory's theory is to predict the temperature dependence of the excess thermodynamic properties from a knowledge of the interaction parameter, X_{12}, at room temperature.

The parameter X_{12} was determined from the excess enthalpy at 298.15 K as described above. By combining Equations (56) and (63), the parameter $\tilde{T}$ can be eliminated and $\tilde{v}$ can be determined. Assuming that X_{12} is independent of temperature, $\tilde{G}^E$, $\tilde{H}^E$, $\tilde{S}^E$, and $\tilde{V}^E$ can be computed as functions of temperature from Equations (59) through (62). The results for equimolar mixtures of n-heptane-toluene and methyl-

cyclohexane-toluene are shown in Table 15, Appendix G, and Figures 9, 10, and 11 (Method 10). For both systems, the predicted excess free energy and enthalpy are practically independent of temperature, in disagreement with experiment. The predicted excess entropy is much too small and decreases with decreasing temperature. The predicted excess volume also decreases with decreasing temperature. Apparently this method of predicting the temperature dependence of the excess thermodynamic properties delivers no better results than the simple assumption that these properties are independent of temperature.

Comparison of the Theories

The results of the preceding sections clearly show that the theory of Rowlinson and Sutton is superior to the others in correlating the excess enthalpy, free energy, and entropy of the systems n-heptane-toluene and methylcyclohexane-toluene. The conformal solution theory and the theory of Flory (both of which assume no orientation-dependent intermolecular forces) fail to represent the temperature dependence of the excess thermodynamic functions even qualitatively. This suggests that directional interactions play an important role in these systems.

For the two systems investigated here, the theory of Rowlinson and Sutton allows a fairly good prediction of $\tilde{H}^E$, $\tilde{G}^E$, and $\tilde{S}^E$ at low temperatures if these data are known at room temperature. More data on aliphatic-aromatic and alicyclic-aromatic mixtures are needed to decide whether this holds for all systems of this type.

The theory of Rowlinson and Sutton has two--comparatively minor--deficiencies:

1. Excess volumes cannot be predicted reliably from the other

excess properties. In this respect, the theory of Flory delivers better results. This is probably due to the fact that the latter theory uses experimental parameters for both pure components and therefore gives a more realistic equation of state for the mixture.

2. The excess enthalpy and entropy of the system n-heptane-toluene below about 220 K show a larger temperature dependence than the corresponding functions of the system methylcyclohexane-toluene. This different behavior is not predicted by the theory of Rowlinson and Sutton. It is interesting to note that the system n-heptane-methylcyclohexane, which is almost ideal at room temperature, shows a strong increase in $\tilde{H}^E$ and $\tilde{S}^E$ in the same temperature region. This suggests that both effects may have the same cause. A possible explanation is presented here in a qualitative manner.

Whereas methylcyclohexane and toluene are relatively rigid molecules, n-heptane is a chain molecule which is quite flexible at sufficiently high temperatures. The molecules alternately coil up, stretch, assume S-shapes, etc. No significant orientation effects would be expected in such a liquid. However, at lower temperatures the molecules become more rigid and assume a more defined shape. They are now more likely to line up with their neighbors in some preferred orientation, similar to the orientation in aromatic liquids assumed in the treatment above. By analogous reasoning, this would explain why n-heptane mixes almost ideally with methylcyclohexane at room temperature, whereas the mixture has a considerable excess enthalpy and entropy at low temperatures. The combination of the attractive orientational forces in toluene and the repulsive orientational forces

in n-heptane would also explain why mixtures of these two components have higher $\tilde{H}^E$ and $\tilde{S}^E$ values at low temperatures than mixtures of methylcyclohexane and toluene.

CHAPTER VII

CONCLUSIONS AND RECOMMENDATIONS

Conclusions

The results of the experimental work may be summarized as follows:

1. The purity of the n-heptane, methylcyclohexane, and toluene samples, as calculated from calorimetric melting point determination, was found to exceed 99.7 mole per cent, which was judged adequate for the purpose of this work. The melting points of the pure substances determined in this study agree within 0.02 K with good literature data, which confirms that the calibration of the thermometer used in this work agrees well with those used in other laboratories.

2. The heat capacities reported in this work generally agree well with literature data of high accuracy. However, the heat capacity of n-heptane measured in this work seems to be, on the average, about 0.15 per cent lower than the literature data. This effect may be at least partly attributed to the impurity in the sample. The accuracy of the heat capacity measurements is estimated to be 0.2 per cent.

3. The density measurements are believed to be accurate to 0.00003 g/cm^3. Deviations from the densities for the pure substances listed in the API Tables[2] exceed this error limit for n-heptane and

toluene. They are attributed to the impurities in the samples used in this work.

The following conclusions are drawn from an analysis of the derived excess thermodynamic properties:

1. The excess heat capacities are believed to be accurate to 0.25 J/mole K. The accuracy of the excess enthalpies varies from 50 J/mole at the lowest temperatures to about 20 J/mole near room temperature. The accuracy of the excess free energies varies from 25 J/mole at the lowest temperatures to 15 J/mole at room temperature. The excess entropy data are accurate within 0.24 J/mole K at the lowest temperatures and 0.12 J/mole K at room temperature. The accuracy of the excess volume data is estimated to be 0.01 cm^3/mole.

2. The systems n-heptane-toluene and methylcyclohexane-toluene show a nearly quadratic dependence of all excess functions on composition. The excess free energy, enthalpy, and entropy increase with decreasing temperature. The temperature dependence of these functions is very similar for both systems, except that below about 220 K the excess enthalpy and entropy increase faster with decreasing temperature for the system n-heptane-toluene than for methylcyclohexane-toluene. The excess volume at room temperature is much smaller for n-heptane-toluene than for methylcyclohexane-toluene.

The equimolar mixture of n-heptane and methylcyclohexane shows very small values of $\tilde{G}^E$, $\tilde{H}^E$, $\tilde{S}^E$, and $\tilde{V}^E$ at room temperature. Below about 240 K, however, $\tilde{H}^E$ and $\tilde{S}^E$ increase rapidly, whereas $\tilde{G}^E$ remains rather small.

The results of the theoretical correlations may be summarized

as follows:

1. The observed temperature dependence of the excess enthalpy, free energy, and entropy of the systems n-heptane-toluene and methylcyclohexane-toluene can be correlated very well using a theory of Rowlinson and Sutton[37] which assumes the presence of orientation-dependent intermolecular forces. The theory permits a prediction of these functions at low temperatures based on room temperature data.

2. The conformal solution theory of Longuet-Higgins[24] and the theory of Flory[15] are unable to correlate the observed temperature dependence of the excess thermodynamic properties. However, the theory of Flory permits a better prediction of the excess volume from the other excess thermodynamic properties than either of the other two theories.

Recommendations for Future Work

1. Excess volumes of the systems studied in this work should be measured over a wide temperature range. Together with the results of this study, this would provide a complete set of the most important excess thermodynamic functions, and it would also furnish a further test for the theories used in this work.

2. Excess thermodynamic functions of other hydrocarbon systems should be studied over a wide range of temperatures. Investigations of other aliphatic-aromatic mixtures (e.g., 2,2,4-trimethylpentane-ethylbenzene) would show whether the behavior of the two systems studied here is typical for this class of mixtures. They would also provide a further test for the theory of Rowlinson and Sutton. Studies

of aliphatic-aliphatic or aromatic-aromatic mixtures (e.g., n-octane-2,2,4-trimethylpentane or toluene-ethylbenzene) would show whether the excess thermodynamic functions of these mixtures show a similar increase at low temperatures as those of the system n-heptane-methylcyclohexane.

APPENDICES

APPENDIX A

TEMPERATURE SCALES AND NUMERICAL CONSTANTS

Temperature Scales

The temperature of the calorimeter can was measured with a platinum resistance thermometer which has been calibrated by the National Bureau of Standards on the International Practical Temperature Scale of 1948 (IPTS-48). This scale is related to the International Practical Kelvin Scale of 1954 (IPKS-54) by the equation

$$T\ (\text{IPKS-54}) = t\ (\text{IPTS-48}) + 273.15 \tag{71}$$

The heat capacities and melting points of the pure components were computed using the IPKS-54 to allow a comparison with literature data, most of which are based on this scale. Prior to 1954, an ice point of 273.16 K was widely used. This shift of 0.01 degrees has no significant influence on the heat capacity data. Melting points reported on this scale were lowered by 0.01 degrees to allow comparisons on the IPKS-54.

For all purposes other than comparisons with literature data, the temperature was converted to the International Practical Temperature Scale of 1968. In order to achieve a consistent nomenclature, this scale will be referred to as the International Practical Kelvin Scale of 1968 (IPKS-68). The difference between the two scales, as listed by Barber[7], was fitted by a tenth degree polynomial over the

range from 93.15 to 373.15 K:

$$t(1968) - t(1954) = 3.96206547\times10^{-4} - 4.91955928\times10^{-4}t + 5.18664917\times10^{-6}t^2 + 4.61114615\times10^{-8}t^3 - 7.33468174\times10^{-10}t^4 - 3.33127229\times10^{-12}t^5 + 4.06683898\times10^{-14}t^6 + 5.11588793\times10^{-16}t^7 + 7.97726901\times10^{-20}t^8 - 2.58971781\times10^{-20}t^9 - 9.27499543\times10^{-23}t^{10} \quad (72)$$

The thermometer used in the density measurements was calibrated by the National Bureau of Standards on the International Temperature Scale of 1927. At 293.15 K, this scale differs from the IPKS-68 by 0.006 degrees. Since the effect of this difference on the density is within the experimental error, no temperature scale corrections were made.

Numerical Constants

Molecular Weights

The molecular weights used in this study were taken from the API Tables[2]. They are based on the C 12 Scale.

n-Heptane	100.206
Methylcyclohexane	98.190
Toluene	92.142

Other Constants

Gas Constant:	R = 8.3143 J/mole K
1 Defined Calorie	= 4.184 J

APPENDIX B

HEAT CAPACITY CALCULATIONS

Sample Calculation of the Heat Capacity of a Mixture

The calculation is made for a mixture of n-heptane (component 1) and toluene (component 2) with a sample weight of 115.405 g (corrected for buoyancy) and a mixture composition of $x_1 = 0.50341$.

The following data were taken in a typical run:

Initial readings on Mueller bridge:

R = 16.09498 ohms

N = 16.19115 ohms

Potentiometer readings:

P = 0.063460 V

Q = 0.085984 V

Heating interval:

t = 1190.16 sec

Final readings on Mueller bridge:

R = 16.61840 ohms

N = 16.71462 ohms

The thermometer resistance, R_t, is found by averaging the two resistance readings on the Mueller bridge:

$$R_t = (R + N)/2 \tag{73}$$

The platinum resistance thermometer has been calibrated by the

National Bureau of Standards on the International Practical Temperature Scale of 1948 (IPTS-48). The temperature was computed from R_t using the equation furnished with the calibration. The temperature was then converted to the International Practical Kelvin Scale of 1968 (IPKS-68) as described in Appendix A. The initial, final, and mean temperature of the measurement were found to be

$T_1 = 182.411$ K

$T_2 = 187.410$ K

$T_m = 184.910$ K

Taking into account the current flowing through the volt box, the power input into the can is given by

$$H = (Q/1.00044 - P/300)(200\ P)(t) \tag{74}$$

For the data reported above,

$H = 1295.07$ J

The heat capacity of the can was measured by Hwa[18] using the International Practical Temperature Scale of 1948 (IPTS-48). His measurements were converted to the IPKS-68 and fitted by the polynomial given in Table 9, Appendix C. From this polynomial, the heat capacity of the can at the mean temperature of the measurement was calculated to be

$C_{p\ can} = 60.99$ J/K

The heat input into the sample is

$$H_{sample} = H - H_{can} = H - C_{p\ can}(T_2 - T_1) \tag{75}$$

For the data reported above,

$$H_{sample} = 990.22 \text{ J}$$

The molecular weight of the mixture is computed from the formula

$$M = x_1 M_1 + x_2 M_2 = 96.201 \text{ g/mole} \tag{76}$$

The number of moles of sample is

$$n = m/M = 1.19962 \text{ moles} \tag{77}$$

The heat capacity of the sample is found to be

$$\tilde{C}_p = H_{sample}/n(T_2 - T_1) = 165.13 \text{ J/mole K} \tag{78}$$

The heat capacity of the pure components at the temperature T_m is computed from the polynomials given in Table 9, Appendix C:

$\tilde{C}_{p1} = 202.36$ J/mole K

$\tilde{C}_{p2} = 135.54$ J/mole K

The excess heat capacity is computed from equation (12):

$\tilde{C}_p^E = -4.04$ J/mole K

Effect of Curvature on the Heat Capacity Data

Formula (5) implies that the approximation

$$C_p(T_m) = \frac{H(T_2) - H(T_1)}{T_2 - T_1} \tag{79}$$

is valid within the experimental accuracy, where T_m is defined as

$$T_m = (T_1 + T_2)/2 \tag{80}$$

To examine the validity of this assumption, $H(T_1)$ and $H(T_2)$ are expanded as Taylor series up to the third-order term:

$$H(T_1) = H(T_m) + (T_1 - T_m)\, H'(T_m) + (1/2)(T_1 - T_m)^2\, H''(T_m) + (1/6)(T_1 - T_m)^3\, H'''(T_m) \tag{81}$$

$$H(T_2) = H(T_m) + (T_2 - T_m)\, H'(T_m) + (1/2)(T_2 - T_m)^2\, H''(T_m) + (1/6)(T_2 - T_m)^3\, H'''(T_m) \tag{82}$$

Equations (81) and (82) are combined to give

$$\frac{H(T_2) - H(T_1)}{T_2 - T_1} = H'(T_m) + (1/24)(T_2 - T_1)^2\, H'''(T_m) \tag{83}$$

If H' is replaced by C_p, Equation (83) becomes

$$\frac{H(T_2) - H(T_1)}{T_2 - T_1} = C_p(T_m) + (1/24)(T_2 - T_1)^2\, C_p''(T_m) \tag{84}$$

Comparison with Equation (79) shows that the approximate value for C_p used in this work differs from the exact value by

$$C_p(\text{approximate}) - C_p(\text{exact}) = (1/24)(T_2 - T_1)^2\, C_p''(T_m) \tag{85}$$

Since the temperature interval $(T_2 - T_1)$ was nearly the same in all measurements (about five degrees), the error depends mainly on C_p'', i.e. the curvature of the heat capacity. Among the substances measured, n-heptane near the triple point shows the greatest curvature effect. For the lowest temperature of measurement, the polynomial given in

Table 9, Appendix C, yields

$$\tilde{C}_p''(185\ K) = 0.01305\ J/mole\ K^3$$

and

$$\tilde{C}_p(approximate) - \tilde{C}_p(exact) = 0.0136\ J/mole\ K$$

This difference is less than 0.01 per cent of the total heat capacity and can therefore be neglected.

Effect of Sample Evaporation on Measured Heat Capacity

During a heat input, the vapor pressure of the sample increases, and some evaporation into the unfilled part of the calorimeter takes place, which increases the measured heat capacity. This effect increases with the vapor pressure of the sample. Below, the error in $\tilde{C}_p$ due to evaporation of the sample is calculated for methylcyclohexane. The vapor pressure curve of n-heptane is virtually identical with that of methylcyclohexane, whereas that of toluene is lower in the temperature region considered here.

The following data are used:

$V = 10\ cm^3$ (Vapor space in calorimeter can)

$T = 310\ K$ (Mean temperature of highest $\tilde{C}_p$ measurement)

$p = 80\ Torr$ (Vapor pressure at 310 K)

$d(\ln P)/dT = 0.0453\ K^{-1}$ (Determined graphically)

$n = 1.19115$ moles (Number of moles in sample)

$\tilde{C}_p = 190\ J/mole\ K$ (Heat capacity of sample at 310 K)

At low pressures, the Clausius-Clapeyron equation can be approximated by

$$\tilde{H}_v = R\,T^2 d(\ln P)/dT \tag{86}$$

Differentiation of the ideal gas law at constant volume yields for the vapor phase

$$\frac{dn}{dT} = \frac{P\,V}{R\,T^2}\left[T\,\frac{d(\ln P)}{dT} - 1\right] \tag{87}$$

The error in the measured heat capacity due to evaporation, ΔC_p, is

$$\Delta C_p = \tilde{H}_v (dn/dT) \tag{88}$$

Changing to molar quantities, Equation (88) becomes

$$\Delta \tilde{C}_p = (1/n)\,\tilde{H}_v\,(dn/dT) \tag{89}$$

Combining Equation (89) with Equations (86) and (87), the error in the heat capacity measurement becomes

$$\Delta C_p = \frac{P\,V}{n}\left[T\,\frac{d(\ln P)}{dT} - 1\right]\frac{d(\ln P)}{dT} \tag{90}$$

For the data given above,

$$\Delta \tilde{C}_p = 0.0512 \text{ J/mole K}$$

The relative error is

$$\Delta \tilde{C}_p / \tilde{C}_p = 2.70\times10^{-4} = 0.027 \text{ per cent}$$

This is considerably less than the total estimated error of the heat capacity measurements. The effect of evaporation was therefore neglected in all heat capacity calculations.

Effect of the Heat Capacity of the Gas Phase

Before the filling operation, the calorimeter can was flushed

with dry nitrogen. After filling, a vapor space of about 10 cm^3 remained above the liquid. The can was sealed at room temperature (about 295 K) and atmospheric pressure. Since the vapor pressure of the samples used was relatively small at room temperature, the gas phase may be considered as essentially pure nitrogen. The heat capacity of nitrogen gas was taken as

$$\tilde{C}_v = 2.5\ R = 20.8\ J/mole\ K$$

Assuming an unfilled space of 10 cm^3, the number of moles of nitrogen is

$$n = PV/RT = 4.0 \times 10^{-4}\ moles$$

The heat capacity of the gas phase is

$$C_v = n\ \tilde{C}_v = 8.3 \times 10^{-3}\ J/K$$

Since the measured sample heat capacity was never below 160 J/K, the heat capacity of the gas phase introduces an error of less than 0.01 per cent, which is completely negligible.

Difference Between $\tilde{C}_p$ and $\tilde{C}_{sat}$

If the effect of sample evaporation and the heat capacity of the gas in the unfilled part of the can are negligible, the measured heat capacity is the heat capacity along the saturation line, $\tilde{C}_{sat}$, rather than the heat capacity at constant pressure, $\tilde{C}_p$. According to Rowlinson (Reference 35, Chapter II), these two quantities are related by the equation

$$\tilde{C}_p - \tilde{C}_{sat} = T\ \tilde{V}\ \alpha\ (dP/dT)_{sat} \qquad (91)$$

For the substances considered here, the difference $(\tilde{C}_p - \tilde{C}_{sat})$ increases with temperature, mainly because of the strong temperature

dependence of $(dP/dT)_{sat}$. Below, a sample calculation is given for methylcyclohexane. The following data are used:

$T = 310$ K (Mean temperature of highest $\tilde{C}_p$ measurement)

$(dP/dT)_{sat} = 4.68 \times 10^{-4}$ J/cm^3 K (Determined graphically)

$\tilde{V} = 130.1$ cm^3/mole (From densities listed in API Tables[2])

$\alpha = 1.153 \times 10^{-3}$ K^{-1} (From densities listed in API Tables[2])

$\tilde{C}_p = 190$ J/mole K (Heat capacity of sample at 310 K)

With these data, Equation (91) yields

$\tilde{C}_p - \tilde{C}_{sat} = 0.0218$ J/mole K

The relative error is

$(\tilde{C}_p - \tilde{C}_{sat})/\tilde{C}_p = 1.15 \times 10^{-4} = 0.0115$ per cent

This error is negligible. Since the values of $\tilde{V}$, α, $(dP/dT)_{sat}$, and $\tilde{C}_p$ for n-heptane and toluene are of the same magnitude as the corresponding values for methylcyclohexane, the error is negligible for these substances, too.

APPENDIX C

HEAT CAPACITY AND DENSITY DATA

Table 8. Experimental Heat Capacity Data

n-Heptane

Sample Weight 104.534 g*

Run No.	Initial T K	Mean T K	$\tilde{C}_p$ J/mole K
304**	182.624	185.004	202.28***
312	183.321	185.480	202.23
305	187.384	189.765	201.68
306	192.145	194.524	201.24
322	195.966	198.446	200.94
307	196.903	199.279	201.06
323	200.926	203.400	201.05
324	205.874	208.341	201.24
325	210.808	213.267	201.71
326	215.725	218.173	202.30
327	220.621	223.059	202.97
328	225.496	227.922	203.75
329	230.349	232.839	204.80
330	235.328	237.824	205.80
331	240.212	242.711	207.08
332	245.210	247.694	208.36
333	250.177	252.644	209.74
334	255.111	257.619	211.08
335	260.126	262.542	212.47
336	264.958	267.377	213.90
337	269.796	272.197	215.57
313	273.113	275.609	216.28
338	274.597	276.982	216.96
314	278.105	280.798	218.12
315	283.492	285.949	219.87
316	288.407	290.846	221.60
318	293.118	295.610	223.20
317	293.286	295.707	223.37
319	298.102	300.503	225.13
320	302.948	305.332	226.84
321	307.716	309.978	228.78

* In vacuo

** Representing chronological order of measurements

*** The last digit has no experimental significance. It is given for reasons of internal consistency and to avoid roundoff errors.

Table 8 - continued

Methylcyclohexane

Sample Weight 116.959 g

Run No.	Initial T K	Mean T K	$\tilde{C}_p$ J/mole K
47*	143.574	146.007	138.82
36	147.107	149.530	139.54
48	148.440	150.912	139.82
37	151.954	154.355	140.51
49	153.383	155.891	140.88
38	156.757	159.138	141.59
50	158.399	160.885	141.91
39	161.518	163.885	142.53
51	163.371	165.853	143.03
40	166.252	168.715	143.60
52	168.336	170.817	144.06
41	171.177	173.619	144.73
53	173.299	175.778	145.24
42	176.060	178.482	145.82
54	178.256	180.734	146.31
43	180.903	183.364	146.91
55	183.212	185.688	147.46
44	185.825	188.264	148.11
56	188.163	190.637	148.61
45	190.704	193.183	149.31
57	193.111	195.582	149.86
46	195.661	198.119	150.56
9	196.876	199.200	150.78
58	198.054	200.524	151.09
10	201.524	203.915	152.15
11	206.307	208.711	153.34
12	211.114	213.497	154.70
13	215.880	218.313	156.07
14	220.747	223.209	157.52
15	225.671	228.155	159.03
16	230.640	233.117	160.64
17	235.595	238.069	162.18
18	240.543	243.012	163.91
19	245.241	247.640	165.53
20	250.038	252.350	167.28
21	254.662	257.031	166.85

*Supercooled Liquid

(continued)

Table 8 - continued

Methylcyclohexane

(Continued)

Sample Weight 116.959 g

Run No.	Initial T K	Mean T K	$\tilde{C}_p$ J/mole K
22	259.401	261.729	170.61
23	264.058	266.371	172.32
24	268.684	270.972	174.18
26	273.122	275.437	175.52
25	273.260	275.478	175.84
27	277.753	280.196	177.43
28	282.639	285.107	179.40
29	287.576	290.068	181.51
31	292.199	294.716	183.29
30	292.560	295.028	183.48
32	297.234	299.726	185.40
33	302.218	304.731	187.67
34	307.245	309.731	189.99

Table 8 - continued

Toluene

Sample Weight 134.016 g

Run No.	Initial T K	Mean T K	$\tilde{C}_p$ J/mole K
72*	162.148	164.413	134.68
73*	166.678	169.054	134.80
74*	171.430	173.798	134.94
75*	176.165	178.524	135.17
67	179.820	181.781	135.34
76	180.882	183.232	135.44
68	183.741	185.968	135.64
69	188.194	190.528	135.98
70	192.862	195.186	136.38
77	195.752	198.169	136.70
71	197.509	199.822	136.86
78	200.586	203.106	137.20
79	205.626	208.132	137.78
80	210.639	213.127	138.52
81	215.615	218.092	139.26
82	220.569	223.032	140.06
83	225.494	227.941	140.85
84	230.388	232.818	141.80
85	235.333	237.746	142.79
86	240.160	242.612	143.78
87	245.064	247.553	144.79
88	250.042	252.513	145.84
89	254.985	257.441	146.81
90	259.896	262.387	147.97
91	264.877	267.350	149.06
92	269.822	272.275	150.34
94	273.399	275.885	151.08
93	274.728	277.165	151.41
95	278.372	280.838	152.39
96	283.305	285.804	153.64
97	288.303	290.782	154.98
99	292.407	294.919	155.98
98	293.261	295.770	156.39
100	297.432	299.923	157.38
101	302.415	304.885	158.92
102	307.355	309.854	160.36

*Supercooled Liquid

Table 8 - continued

System n-Heptane-Toluene

Mixture Composition 0.18810 Mole Fraction n-Heptane

Sample Weight 122.747 g

Run No.	Initial T K	Mean T K	$\tilde{C}_p$ J/mole K	$\tilde{C}_p^E$ J/mole K
433	182.382	184.830	145.20	-2.90
434	187.279	189.717	145.50	-2.78
435	192.155	194.582	145.95	-2.60
437	195.156	197.689	146.13	-2.65
436	197.009	199.424	146.41	-2.51
438	200.221	202.740	146.74	-2.48
439	205.259	207.764	147.39	-2.37
440	210.269	212.760	148.16	-2.22
441	215.250	217.726	148.90	-2.18
442	220.202	222.662	149.84	-2.01
443	225.122	227.567	150.72	-1.96
444	230.012	232.440	151.77	-1.78
454	234.850	237.381	152.74	-1.77
455	239.912	242.422	153.97	-1.56
456	244.932	247.423	155.17	-1.43
457	249.914	252.387	156.42	-1.29
458	254.859	257.313	157.57	-1.28
459	259.767	262.202	158.81	-1.20
460	264.638	267.057	159.91	-1.31
461	269.476	271.876	161.25	-1.19
445	274.002	276.387	162.16	-1.45
462	274.276	276.660	162.31	-1.37
446	278.772	281.137	163.57	-1.31
447	283.503	285.852	164.95	-1.21
448	288.200	290.641	166.39	-1.10
450	292.974	295.396	167.67	-1.17
449	293.082	295.393	167.83	-1.01
451	297.818	300.328	169.28	-0.99
452	302.839	305.219	170.90	-0.81
453	307.600	310.068	172.52	-0.64

Table 8 - continued

System n-Heptane-Toluene

Mixture Composition 0.34751 Mole Fraction n-Heptane

Sample Weight 119.713 g

Run No.	Initial T K	Mean T K	$\tilde{C}_p$ J/mole K	$\tilde{C}_p^E$ J/mole K
369	182.209	184.735	154.96	-3.80
370	187.261	189.651	155.12	-3.63
371	192.042	194.422	155.52	-3.36
382	195.625	198.108	155.77	-3.30
372	196.803	199.175	155.80	-3.33
383	200.591	203.062	156.36	-3.06
384	205.532	207.991	156.92	-2.97
385	210.450	212.895	157.65	-2.81
386	215.341	217.772	158.42	-2.71
387	220.204	222.743	159.28	-2.60
388	225.282	227.805	160.20	-2.55
389	230.328	232.834	161.33	-2.34
390	235.340	237.827	162.44	-2.23
391	240.288	242.756	163.48	-2.23
392	245.224	247.673	164.80	-2.00
393	250.122	252.553	166.09	-1.84
394	254.984	257.398	167.22	-1.88
395	259.813	262.209	168.58	-1.72
396	264.605	266.983	169.87	-1.65
397	269.362	271.723	171.17	-1.61
373	273.157	275.618	172.01	-1.83
398	274.084	276.429	172.34	-1.72
374	278.079	280.595	173.48	-1.73
375	283.110	285.605	175.03	-1.60
376	288.100	290.575	176.63	-1.44
378	292.956	295.447	177.96	-1.56
377	293.050	295.540	178.23	-1.33
379	297.938	300.408	179.63	-1.40
380	302.879	305.328	181.25	-1.32
381	307.778	310.207	182.92	-1.21

Table 8 - continued

System n-Heptane-Toluene

Mixture Composition 0.50341 Mole Fraction n-Heptane

Sample Weight 115.405 g

Run No.	Initial T K	Mean T K	$\tilde{C}_p$ J/mole K	$\tilde{C}_p^E$ J/mole K
339	182.411	184.910	165.13	-4.04
340	187.410	189.902	165.15	-3.84
341	192.396	194.879	165.44	-3.56
352	195.037	197.500	165.63	-3.44
342	197.363	199.711	165.87	-3.30
353	199.962	202.414	166.09	-3.23
354	204.865	207.387	166.72	-2.99
355	209.909	212.417	167.44	-2.80
356	214.925	217.440	168.26	-2.63
357	219.955	222.476	169.08	-2.57
358	224.996	227.502	170.09	-2.41
359	230.008	232.497	171.10	-2.34
360	234.987	237.459	172.22	-2.22
361	239.932	242.387	173.45	-2.06
362	244.829	247.267	174.61	-2.01
363	249.705	252.125	175.90	-1.89
364	254.546	256.951	177.08	-1.92
365	259.356	261.858	178.47	-1.79
366	264.360	266.842	179.87	-1.72
367	269.325	271.788	181.39	-1.56
343	273.138	275.584	182.20	-1.81
368	274.252	276.588	182.59	-1.72
344	278.030	280.531	183.76	-1.68
345	283.031	285.549	185.34	-1.58
346	288.068	290.565	187.01	-1.44
348	292.823	295.300	188.41	-1.51
347	293.062	295.541	188.59	-1.40
349	297.778	300.235	190.12	-1.37
350	302.692	305.201	191.83	-1.29
351	307.709	310.125	193.60	-1.19

Table 8 - continued

System n-Heptane-Toluene

Mixture Composition 0.66119 Mole Fraction n-Heptane

Sample Weight 110.229 g

Run No.	Initial T K	Mean T K	$\tilde{C}_p$ J/mole K	$\tilde{C}_p^E$ J/mole K
463	182.581	184.946	176.04	-3.66
464	187.311	189.671	175.96	-3.41
465	192.031	194.384	176.15	-3.07
467	195.663	198.119	176.31	-2.94
466	196.737	199.083	176.37	-2.89
468	200.574	203.020	176.70	-2.73
469	205.467	207.903	177.19	-2.57
470	210.339	212.764	177.85	-2.39
471	215.188	217.601	178.57	-2.28
472	220.014	222.414	179.39	-2.18
473	224.814	227.201	180.24	-2.14
474	229.588	232.080	181.31	-1.99
475	234.571	237.048	182.39	-1.93
476	239.524	241.983	183.67	-1.75
477	244.484	246.923	184.89	-1.69
478	249.362	251.784	186.20	-1.58
479	254.206	256.613	187.42	-1.61
480	259.019	261.522	188.87	-1.47
481	264.025	266.509	190.27	-1.45
482	268.994	271.459	191.90	-1.22
484	272.870	275.433	192.88	-1.41
483	273.924	276.373	193.18	-1.38
485	277.997	280.540	194.53	-1.28
486	283.082	285.605	196.24	-1.13
487	288.127	290.631	197.77	-1.19
489	292.840	295.325	199.23	-1.25
488	293.135	295.402	199.35	-1.16
490	297.810	300.274	201.04	-1.10
491	302.739	305.183	202.80	-1.04
492	307.627	310.051	204.55	-1.02

Table 8 - continued

System n-Heptane-Toluene

Mixture Composition 0.82359 Mole Fraction n-Heptane

Sample Weight 107.904 g

Run No.	Initial T K	Mean T K	$\tilde{C}_p$ J/mole K	$\tilde{C}_p^E$ J/mole K
399	182.346	184.654	188.14	-2.45
400	186.961	189.388	187.76	-2.30
401	191.816	194.238	187.75	-2.02
403	195.545	198.069	187.72	-1.98
402	196.661	198.955	187.82	-1.87
404	200.594	203.109	188.08	-1.70
405	205.625	208.131	188.47	-1.60
406	210.638	213.133	189.07	-1.46
407	215.628	218.112	189.71	-1.42
408	220.596	223.068	190.54	-1.34
409	225.539	227.997	191.47	-1.27
410	230.455	232.898	192.56	-1.14
411	235.341	237.770	193.64	-1.10
412	240.199	242.612	194.88	-0.98
413	244.976	247.486	196.07	-0.98
414	249.996	252.488	197.48	-0.86
415	254.980	257.456	198.74	-0.93
416	259.932	262.391	200.12	-0.92
417	264.850	267.292	201.51	-0.95
418	269.734	272.158	203.15	-0.75
420	273.004	275.526	203.96	-0.97
419	274.581	276.768	204.51	-0.80
421	278.048	280.550	205.68	-0.81
422	283.052	285.644	207.38	-0.74
423	288.235	290.699	209.13	-0.65
425	293.000	295.445	210.68	-0.72
424	293.162	295.606	210.90	-0.55
426	297.890	300.315	212.53	-0.57
427	302.740	305.252	214.31	-0.58
428	307.763	310.150	216.18	-0.55

Table 8 - continued

System Methylcyclohexane-Toluene

Mixture Composition 0.16728 Mole Fraction Methylcyclohexane

Sample Weight 129.556 g

Run No.	Initial T K	Mean T K	$\tilde{C}_p$ J/mole K	$\tilde{C}_p^E$ J/mole K
208	162.039	164.384	134.74	-1.27
209	166.728	169.248	134.98	-1.27
210	171.767	174.275	135.27	-1.31
211	176.782	179.278	135.65	-1.32
212	181.774	184.257	136.09	-1.34
213	186.740	189.210	136.56	-1.38
214	191.680	194.136	137.15	-1.37
216	196.403	198.712	137.63	-1.47
215	196.592	199.035	137.75	-1.40
217	201.022	203.435	138.36	-1.40
218	205.848	208.306	139.03	-1.45
219	210.764	213.207	139.85	-1.42
220	215.649	218.134	140.69	-1.43
221	220.618	223.086	141.64	-1.38
222	225.553	228.041	142.61	-1.36
223	230.530	233.018	143.71	-1.26
224	235.506	237.994	144.84	-1.17
225	240.482	242.968	146.08	-1.02
226	245.441	247.912	146.95	-1.28
227	250.382	252.849	148.34	-1.05
228	255.316	257.783	149.48	-1.12
229	260.250	262.716	150.68	-1.15
230	265.183	267.630	151.94	-1.16
231	270.076	272.537	153.41	-0.99
233	273.278	275.760	154.11	-1.16
232	274.998	277.299	154.64	-1.05
234	278.241	280.719	155.49	-1.14
235	283.197	285.670	157.01	-1.01
236	288.144	290.613	158.51	-0.93
237	293.083	295.548	160.01	-0.87
238	293.229	295.694	159.92	-1.01
239	298.158	300.618	161.47	-0.91
240	303.078	305.533	163.12	-0.74
241	307.987	310.435	164.80	-0.56

Table 8 - continued

System Methycyclohexane-Toluene

Mixture Composition 0.31372 Mole Fraction Methylcyclohexane

Sample Weight 124.780 g

Run No.	Initial T K	Mean T K	$\tilde{C}_p$ J/mole K	$\tilde{C}_p^E$ J/mole K
139	162.012	164.430	135.64	-1.53
140	166.848	169.317	136.00	-1.56
141	171.786	174.306	136.34	-1.68
142	176.826	179.334	136.69	-1.86
143	181.842	184.335	137.26	-1.87
144	186.828	189.306	137.87	-1.91
145	191.785	194.248	138.60	-1.87
147	195.335	197.832	138.99	-2.02
146	196.710	199.158	139.28	-1.93
148	200.330	202.831	139.80	-2.01
149	205.333	207.838	140.64	-2.02
150	210.342	212.850	141.55	-2.02
151	215.357	217.867	142.52	-2.01
152	220.376	222.887	143.57	-1.97
153	225.398	227.910	144.65	-1.96
154	230.422	232.932	145.89	-1.82
155	235.443	237.953	147.08	-1.79
156	240.463	242.970	148.46	-1.60
157	245.593	248.082	149.60	-1.73
158	250.572	253.058	151.01	-1.59
159	255.545	258.029	152.41	-1.50
160	260.514	262.996	153.76	-1.50
161	256.478	267.959	155.10	-1.53
162	270.439	272.915	156.73	-1.32
164	274.250	276.725	157.46	-1.70
163	275.390	277.864	158.11	-1.38
165	279.200	281.492	159.07	-1.51
166	283.784	286.270	160.49	-1.52
167	288.754	291.235	162.14	-1.42
169	292.938	295.435	163.25	-1.62
168	293.715	296.192	163.67	-1.44
170	297.932	300.405	165.03	-1.43
171	302.879	305.329	166.81	-1.23
172	307.779	310.207	168.54	-1.11

Table 8 - continued

System Methylcyclohexane-Toluene

Mixture Composition 0.53541 Mole Fraction Methylcyclohexane

Sample Weight 119.421 g

Run No.	Initial T K	Mean T K	$\tilde{C}_p$ J/mole K	$\tilde{C}_p^E$ J/mole K
104	161.973	164.476	137.34	-1.59
105	166.979	169.467	137.83	-1.71
106	171.955	174.428	138.36	-1.85
107	176.902	179.360	138.97	-1.96
108	181.818	184.324	139.71	-1.98
109	186.829	189.319	140.44	-2.09
110	191.809	194.281	141.32	-2.09
112	195.702	198.208	141.85	-2.28
111	196.753	199.208	142.15	-2.17
113	200.714	203.201	142.89	-2.22
114	205.687	208.157	143.84	-2.29
115	210.626	213.076	144.97	-2.21
116	215.526	218.019	146.05	-2.24
117	220.512	222.985	147.24	-2.20
118	225.458	227.912	148.43	-2.21
119	230.366	232.857	149.82	-2.06
120	235.349	237.822	151.17	-2.00
121	240.295	242.744	152.65	-1.84
122	245.106	247.592	153.97	-1.86
123	250.077	252.541	155.50	-1.74
124	255.004	257.447	156.92	-1.75
125	259.889	262.366	158.48	-1.66
126	264.842	267.298	159.98	-1.68
127	269.754	272.241	161.69	-1.51
129	273.678	276.147	162.57	-1.89
128	274.728	277.195	163.18	-1.62
130	278.617	281.062	164.34	-1.73
131	283.508	285.986	166.06	-1.65
132	288.463	290.917	167.87	-1.52
134	292.521	294.956	169.12	-1.67
133	293.371	295.802	169.62	-1.46
135	297.391	299.856	170.95	-1.55
136	302.321	304.813	172.88	-1.40
137	307.306	309.774	174.84	-1.24

Table 8 - continued

System Methylcyclohexane-Toluene

Mixture Composition 0.66700 Mole Fraction Methycyclohexane

Sample Weight 120.148 g

Run No.	Initial T K	Mean T K	$\tilde{C}_p$ J/mole K	$\tilde{C}_p^E$ J/mole K
174	161.862	164.355	138.29	-1.66
175	166.848	169.323	138.99	-1.71
176	171.799	174.259	139.65	-1.82
177	176.718	179.225	140.42	-1.90
178	181.731	184.220	141.27	-1.93
179	186.708	189.179	142.12	-2.02
180	191.650	194.101	143.11	-2.00
182	196.227	198.711	143.88	-2.18
181	196.553	198.988	144.00	-2.12
183	201.194	203.658	145.01	-2.13
184	206.123	208.568	146.06	-2.18
185	211.014	213.500	147.29	-2.11
186	215.986	218.452	148.52	-2.09
187	220.918	223.365	149.73	-2.11
188	225.811	228.297	151.01	-2.12
189	230.782	233.246	152.47	-2.00
190	235.709	238.151	153.91	-1.92
191	240.593	243.012	155.44	-1.79
192	244.818	247.333	156.68	-1.81
193	249.848	252.339	158.33	-1.67
194	254.830	257.302	159.68	-1.85
195	259.774	262.222	161.39	-1.71
196	264.670	267.096	163.01	-1.67
197	269.522	271.924	164.79	-1.49
199	273.192	275.683	165.84	-1.71
198	274.327	276.708	166.32	-1.58
200	278.174	280.660	167.61	-1.66
201	283.145	285.624	169.48	-1.54
202	288.104	290.578	171.28	-1.51
204	292.687	295.172	172.88	-1.58
203	293.052	295.519	173.22	-1.38
205	297.658	300.137	174.85	-1.46
206	302.615	305.086	176.86	-1.32
207	307.556	310.020	178.88	-1.20

Table 8 - continued

System Methylcyclohexane-Toluene

Mixture Composition 0.82676 Mole Fraction Methylcyclohexane

Sample Weight 120.677 g

Run No.	Initial T K	Mean T K	$\tilde{C}_p$ J/mole K	$\tilde{C}_p^E$ J/mole K
242	162.010	164.427	139.98	-1.26
243	166.844	169.306	140.85	-1.26
244	171.769	174.234	141.72	-1.32
245	176.700	179.146	142.60	-1.41
246	181.591	184.060	143.58	-1.44
247	186.529	189.001	144.51	-1.57
248	191.472	193.945	145.60	-1.59
250	195.810	198.289	146.66	-1.53
249	196.417	198.891	146.70	-1.64
251	200.768	203.247	147.84	-1.55
252	205.726	208.206	148.98	-1.64
253	210.685	213.164	150.31	-1.59
254	215.642	218.119	151.61	-1.60
255	220.597	223.072	152.98	-1.59
256	225.548	228.023	154.35	-1.62
257	230.497	232.968	155.89	-1.52
258	235.439	237.908	157.40	-1.49
259	240.397	242.859	159.00	-1.41
260	245.321	247.780	160.49	-1.47
261	250.240	252.694	162.24	-1.31
262	255.147	257.598	163.82	-1.35
263	260.048	262.493	165.61	-1.22
264	264.937	267.378	167.26	-1.26
265	269.818	272.252	169.22	-1.02
267	273.199	275.705	170.28	-1.21
266	274.685	277.115	170.86	-1.15
268	278.210	280.708	172.25	-1.07
269	283.206	285.698	174.10	-1.10
270	288.190	290.674	176.06	-1.03
272	292.886	295.365	177.77	-1.15
271	293.158	295.635	178.09	-0.93
273	297.843	300.313	179.84	-1.04
274	302.783	305.245	181.89	-0.98
275	307.708	310.160	184.11	-0.78

Table 8 - continued

System n-Heptane-Methylcyclohexane

Mixture Composition 0.48910 Mole Fraction n-Heptane

Sample Weight 108.964 g

Run No.	Initial T K	Mean T K	$\tilde{C}_p$ J/mole K	$\tilde{C}_p^E$ J/mole K
506	182.478	184.973	168.89	-5.29
507	187.467	189.815	169.66	-4.78
508	192.163	194.497	170.54	-4.30
510	194.906	197.347	171.00	-4.15
509	196.830	199.151	171.34	-4.03
511	199.788	202.211	172.00	-3.79
512	204.635	207.170	173.11	-3.45
513	209.704	212.220	174.30	-3.18
514	214.736	217.233	175.57	-2.92
515	219.730	222.209	176.92	-2.68
516	224.687	227.147	178.26	-2.52
517	229.607	232.047	179.78	-2.25
518	234.487	237.029	181.29	-2.09
519	239.572	242.093	182.91	-1.91
520	244.465	246.964	184.37	-1.88
521	249.464	251.942	186.04	-1.74
522	254.421	256.878	187.66	-1.68
523	259.336	261.773	189.46	-1.47
524	264.209	266.741	191.16	-1.43
525	269.273	271.667	193.08	-1.19
527	273.190	275.680	194.36	-1.32
526	274.060	276.435	194.74	-1.21
528	278.171	280.639	196.29	-1.17
529	283.108	285.555	198.19	-1.08
530	288.002	290.537	200.22	-0.91
532	292.769	295.173	201.90	-1.02
531	293.073	295.476	202.20	-0.84
533	297.578	300.069	203.97	-0.88
534	302.561	305.137	206.09	-0.82
535	307.714	310.158	208.34	-0.66

Table 9. List of Polynomials Representing the Heat Capacity Data of the Pure Substances and of the Calorimeter Can

The polynomial,

$$C_p = a_o + a_1 T + a_2 T^2 + a_3 T^3 + a_4 T^4 \qquad (93)$$

(Units: J, mole, K) is used to represent the experimental heat capacity data of the pure substances (given in Table 8) and of the calorimeter can.

	Calorimeter Can	n-Heptane	Methylcyclohexane	Toluene
		IPKS-54*		
a_o	-7.7787759(+0)**	8.6131284(+2)	8.4378399(+1)	2.2722844(+2)
a_1	8.6154955(-1)	-9.8531424(+0)	7.9121196(-1)	-1.4178301(+0)
a_2	-4.1152165(-3)	5.3753356(-2)	-4.9163342(-3)	7.3902325(-3)
a_3	9.4601731(-6)	-1.2838133(-4)	1.6721646(-5)	-1.5461866(-5)
a_4	-8.2160413(-9)	1.1703208(-7)	-1.7919852(-8)	1.3324704(-8)
z***		0.0743	0.0901	0.0652
		IPKS-68*		
a_o	-3.0881748(+0)	8.6618820(+2)	1.2988277(+2)	1.8743814(+2)
a_1	7.7257640(-1)	-9.9628490(+0)	-5.4107773(-2)	-7.3026493(-1)
a_2	-3.5143822(-3)	5.4561085(-2)	7.9975642(-4)	2.9613602(-3)
a_3	7.7336026(-6)	-1.3079634(-4)	0	-2.8661704(-6)
a_4	-6.4189154(-9)	1.1957392(-7)	0	0
z***	0.0360	0.0745	0.1045	0.0748

* See Appendix A for definition of temperature scales.

** Numbers in parentheses indicate the power of ten by which the coefficients have to be multiplied.

*** z denotes the standard deviation, which is defined by Equation (8) (Unit: J/mole K).

Table 10. Comparison of the Heat Capacities of the Pure Substances With Literature Data (IPKS-54)*

Methylcyclohexane

T	$\tilde{C}_p$ (this work)	$\tilde{C}_p$(literature) - $\tilde{C}_p$(this work)	
K	J/mole K	J/mole K	
		Douslin and Huffman[13]	Hwa[18]
150	139.81	0.10	
160	141.86	0.14	
170	143.99	0.19	
180	146.22	0.22	0.26
190	148.57	0.21	0.23
200	151.07	0.14	0.23
210	153.73	0.07	0.24
220	156.57	0.04	0.25
230	159.59	0.11	0.26
240	162.79	0.22	0.25
250	166.19	0.25	0.23
260	169.76	0.19	0.21
270	173.50	0.14	0.19
280	177.41	-0.01	0.19
290	181.45	-0.16	0.22
300	185.61		0.31
310	189.86		

* See Appendix A for definition of temperature scales

Table 10 - continued

n-Heptane

T	$\tilde{C}_p$ (this work)	$\tilde{C}_p$(literature) - $\tilde{C}_p$ (this work)		
K	J/mole K	J/mole K		
		McCullough and Messerly[27]	Douglas et al.[12]	Brown[10]
190	201.66	0.30	0.22	0.02
200	201.02	0.44	0.27	-0.01
210	201.34	0.45	0.32	0.01
220	202.43	0.45	0.32	0.00
230	204.13	0.38	0.21	0.04
240	206.29	0.32	0.19	-0.11
250	208.81	0.31	0.14	-0.16
260	211.60	0.36	0.11	-0.15
270	214.61	0.41	0.20	-0.06
280	217.81	0.55	0.42	0.12
290	221.21	0.71	0.54	0.33
300	224.84	0.80	0.59	0.46
310	228.74	0.75	0.54	

Toluene

T	$\tilde{C}_p$ (this work)	$\tilde{C}_p$(literature) - $\tilde{C}_p$(this work)	
K	J/mole K	J/mole K	
		Scott et al.[41]	Hwa[18]
180	135.28	0.36	0.25
190	135.94	0.26	0.05
200	136.90	0.15	-0.01
210	138.12	0.05	0.02
220	139.57	-0.01	0.05
230	141.23	-0.05	0.14
240	143.09	-0.06	0.18
250	145.12	-0.04	0.19
260	147.31	0.01	0.16
270	149.64	0.08	0.12
280	152.11	0.17	0.09
290	154.72	0.25	0.10
300	157.46	0.31	0.20
310	160.33	0.35	

Table 11. Density and Excess Volume Data

x_1	ρ g/cm^3	$\tilde{V}$ cm^3/mole	$\tilde{V}^E$ cm^3/mole
	System n-Heptane(1)-Toluene		
0.00000	0.86648	106.341	0.000
0.18810	0.82166	113.987	0.087
0.34751	0.78833	120.438	0.132
0.50341	0.75918	126.717	0.145
0.66119	0.73264	133.046	0.134
0.82359	0.70800	139.526	0.087
1.00000	0.68387	146.528	0.000
	System Methylcyclohexane(1)-Toluene		
0.00000	0.86648	106.341	0.000
0.16728	0.84607	110.102	0.202
0.31372	0.82975	113.334	0.319
0.53541	0.80747	118.122	0.389
0.66700	0.79557	120.889	0.357
0.82676	0.78231	124.174	0.243
1.00000	0.76941	127.617	0.000
	System n-Heptane(1)-Methylcyclohexane		
0.00000	0.76941	127.617	0.000
0.48910	0.72468	136.855	-0.011
1.00000	0.68387	146.528	0.000

APPENDIX D

EXTRAPOLATION OF $\tilde{G}^E$ FOR THE SYSTEM METHYLCYCLOHEXANE-TOLUENE

Schneider[40] has determined the excess free energy of the system methylcyclohexane-toluene at 333.15; 353.15; 363.15; and 373.15 K. No other measurements could be found in the literature. Since the heat capacity measurements of this work only cover the range up to 312 K, an extrapolation procedure has to be used in order to determine the integration constants necessary for the computation of the excess free energy. Below, two possible extrapolation procedures are described and their results are compared.

1. The $\tilde{G}^E$ data are extrapolated to 312 K and used as integration constants at that temperature. For this purpose, Schneider's data were fitted to two-constant Redlich-Kister equations,

$$\tilde{G}^E = x_1 x_2 [C_o + C_1(x_1 - x_2)] \tag{93}$$

The constants C_o and C_1 are given in Table 6, Chapter V. A plot of C_o and C_1 showed that they can be represented by straight lines within the accuracy of the data. From this plot, the constants at 312 K were found to be

$C_o = 927.30$ J/mole

$C_1 = -57.95$ J/mole

Table 12 shows the $\tilde{G}^E$ data at 312 K determined by this method.

2. The $\tilde{C}_p^E$ data are extrapolated to 333.15 K using the equation given in Table 13, Appendix E. Schneider's $\tilde{G}^E$ data at 333.15 K are

Table 12. Comparison of Extrapolation Methods for $\tilde{G}^E$ of Methylcyclohexane-Toluene (T = 312 K)

x_1	G^E (Method 1) J/mole	G^E (Method 2) J/mole
0.1	87.6	86.7
0.2	153.9	152.8
0.3	199.6	198.6
0.4	225.3	224.6
0.5	231.8	231.3
0.6	219.8	219.3
0.7	189.9	189.4
0.8	142.8	142.3
0.9	79.3	78.8

used as integration constants. The $\tilde{G}^E$ data at 312 K obtained by this method are also listed in Table 12.

The excess free energy data at 312 K derived from methods 1 and 2 agree very well, with a maximum difference of slightly more than 1 J/mole K. Since the two sets of data were obtained by entirely different methods, this is a good indication that the extrapolation does not affect the accuracy of the derived excess free energy data significantly. Method 2 has the advantage that the extrapolated data are integrated twice to obtain $\tilde{G}^E$. Any errors due to the extrapolation are therefore likely to have a very small effect on $\tilde{G}^E$, which is the reason why the second method was selected for this work.

APPENDIX E

DERIVED EXCESS THERMODYNAMIC PROPERTIES

Table 13. Functions Representing the Derived Excess Thermodynamic Properties

System n-Heptane(1)-Toluene

Temperature Range 182 to 312 K

Units: J, mole, cm^3, K

$$\tilde{G}^E = x_1x_2 [(16451.814 - 843.97284\ T - 0.8360739\ T^2 + 9.7291136\times10^{-4}\ T^3 - 5.8287258\times10^{-7}\ T^4 + 170.41964\ T\ \ln T) + (- 1040.0338 + 16.374678\ T - 2.318104\ T\ \ln T)(x_1 - x_2) + (527.75221 - 9.6607141\ T + 1.384904\ T\ \ln T)(x_1 - x_2)^2]$$

$$\tilde{H}^E = x_1x_2 [(16451.814 - 170.41964\ T + 0.8360739\ T^2 - 1.94582273\times10^{-3}\ T^3 + 1.74861875\times10^{-6}\ T^4) + (- 1040.0338 + 2.318104\ T)(x_1 - x_2) + (527.75221 - 1.384904\ T)(x_1 - x_2)^2]$$

$$\tilde{S}^E = x_1x_2 [(673.5532 + 1.6721478\ T - 2.9187341\times10^{-3}\ T^2 + 2.3314903\times10^{-6}\ T^3 - 170.41964\ \ln T) + (- 14.056574 + 2.318104\ \ln T)(x_1 - x_2) + (8.2758101 - 1.384904\ \ln T)(x_1 - x_2)^2]$$

$$\tilde{C}_p^{\ E} = x_1x_2 [(- 170.41964 + 1.6721478\ T - 5.8374682\times10^{-3}\ T^2 + 6.9944750\times10^{-6}\ T^3) + 2.318104\ (x_1 - x_2) - 1.384904\ (x_1 - x_2)^2]$$

$$\tilde{V}^E = x_1x_2 [0.58544 + 2.532\times10^{-2}\ (x_1 - x_2)]$$

(293.15 K)

Table 13 - continued

System Methylcyclohexane(1)-Toluene

Temperature Range 162 to 312 K

Units: J, mole, cm^3, K

$$\tilde{G}^E = x_1 x_2 [(- 639.4904 + 342.53415\ T + 0.53712445\ T^2 - 7.1421085 \times 10^{-4}\ T^3 + 4.5461617 \times 10^{-7}\ T^4 - 78.249165\ T\ \ln T) + (65.078891 - 3.6981461\ T + 0.577025\ T\ \ln T)(x_1 - x_2) + (954.67449 - 22.449973\ T + 3.371621\ T\ \ln T)(x_1 - x_2)^2]$$

$$\tilde{H}^E = x_1 x_2 [(- 639.4904 + 78.249165\ T - 0.53712445\ T^2 + 1.4284217 \times 10^{-3}\ T^3 - 1.3638485 \times 10^{-6}\ T^4) + (65.078891 - 0.577025\ T)(x_1 - x_2) + (954.67449 - 3.371621\ T)(x_1 - x_2)^2]$$

$$\tilde{S}^E = x_1 x_2 [(- 264.28498 - 1.0742489\ T + 2.14263255 \times 10^{-3}\ T^2 - 1.8184647 \times 10^{-6}\ T^3 + 78.249165\ \ln T) + (3.1211211 - 0.577025\ \ln T)(x_1 - x_2) + (19.078352 - 3.371621\ \ln T)(x_1 - x_2)^2]$$

$$\tilde{C}_p^{\ E} = x_1 x_2 [(78.249165 - 1.0742489\ T + 4.285265 \times 10^{-3}\ T^2 - 5.4553939 \times 10^{-6}\ T^3 - 0.577025\ (x_1 - x_2) - 3.371621\ (x_1 - x_2)^2]$$

$$\tilde{V}^E = x_1 x_2 [1.55397 + 0.18259\ (x_1 - x_2)]$$

(293.15 K)

Table 13 - continued

System n-Heptane(1)-Methylcyclohexane

Temperature Range 182 to 312 K

Mixture Composition 0.48910 Mole Fraction n-Heptane

Units: J, mole, cm^3, K

$$\tilde{G}^E = 5370.5959 - 330.60088\ T - 0.33652798\ T^2 + 3.8757364 \times 10^{-4}\ T^3 - 2.2840533 \times 10^{-7}\ T^4 + 67.489297\ T\ \ln T$$

$$\tilde{H}^E = 5370.5959 - 67.489297\ T + 0.33652798\ T^2 - 7.7514727 \times 10^{-4}\ T^3 + 6.8521600 \times 10^{-7}\ T^4$$

$$\tilde{S}^E = 263.11158 + 0.67305596\ T - 1.16272091 \times 10^{-3} + 9.1362133 \times 10^{-7}\ T^3 - 67.489297\ \ln T$$

$$\tilde{C}_p^{\ E} = - 67.489297 + 0.67305597\ T - 2.3254418 \times 10^{-3}\ T^2 + 2.7408640 \times 10^{-6}\ T^3$$

$$\tilde{V}^E = - 0.011$$

(293.15 K)

Table 14. Derived Excess Thermodynamic Properties

System n-Heptane-Toluene

	Mole Fraction n-Heptane								
	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9
T, K	Excess Gibbs Free Energy, J/mole								
180.00*	186.1	318.8	404.0	446.9	451.7	422.0	360.4	269.0	148.7
190.00	176.8	303.3	385.0	426.3	431.4	403.3	344.7	257.3	142.2
200.00	168.3	289.3	367.7	407.8	413.1	386.6	330.5	246.8	136.4
210.00	160.6	276.5	352.1	391.0	396.5	371.4	317.7	237.3	131.2
220.00	153.5	264.8	337.7	375.6	381.4	357.5	306.1	228.7	126.4
230.00	146.9	254.0	324.5	361.4	367.5	344.8	295.4	220.7	122.0
240.00	140.9	244.0	312.2	348.3	354.6	333.0	285.5	213.4	117.9
250.00	135.2	234.7	300.8	336.1	342.6	322.1	276.3	206.6	114.2
260.00	130.0	226.0	290.2	324.7	331.4	311.8	267.7	200.2	110.7
270.00	125.1	217.9	280.3	314.0	320.9	302.2	259.6	194.3	107.4
280.00	120.5	210.3	270.9	304.0	311.0	293.2	252.0	188.7	104.3
290.00	116.2	203.2	262.2	294.6	301.7	284.7	244.9	183.4	101.4
298.15**	112.9	197.7	255.4	287.3	294.5	278.1	239.3	179.3	99.1
300.00	112.2	196.5	253.9	285.7	292.9	276.7	238.1	178.4	98.6
310.00	108.4	190.1	246.1	277.3	284.6	269.0	231.6	173.6	96.0
320.00*	104.8	184.2	238.7	269.2	276.6	261.6	225.4	169.0	93.5

* Extrapolated

** Surovy and Heinrich[45] (Integration constants)

Table 14 - continued

System n-Heptane-Toluene

	Mole Fraction n-Heptane								
	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9
T, K	Excess Enthalpy, J/mole								
180.00*	362.6	612.3	765.7	837.2	838.2	777.4	661.1	492.7	272.9
190.00	345.2	582.7	728.5	796.1	796.7	738.6	627.7	467.6	258.9
200.00	329.7	556.5	695.7	760.2	760.5	704.8	598.8	445.8	246.7
210.00	315.8	533.2	666.6	728.4	728.8	675.3	573.6	426.9	236.2
220.00	303.2	512.1	640.6	700.2	700.6	649.3	551.5	410.4	226.9
230.00	291.7	493.1	617.1	674.8	675.5	626.2	531.9	395.7	218.7
240.00	281.1	475.5	595.6	651.8	652.8	605.4	514.3	382.6	211.5
250.00	271.2	459.2	575.8	630.7	632.1	586.5	498.4	370.8	204.9
260.00	261.9	444.0	557.3	611.2	613.1	569.2	483.9	360.0	198.9
270.00	253.0	429.7	540.1	592.9	595.4	553.2	470.5	350.1	193.4
280.00	244.6	416.1	523.9	575.9	578.9	538.4	458.2	341.1	188.3
290.00	236.7	403.4	508.7	560.0	563.7	524.7	446.9	332.7	183.7
298.15**	230.6	393.6	497.1	548.0	552.3	514.5	438.5	326.6	180.3
300.00	229.2	391.4	494.5	545.4	549.8	512.3	436.7	325.3	179.6
310.00	222.2	380.4	481.7	532.2	537.3	501.3	427.7	318.7	176.0
320.00*	215.9	370.5	470.2	520.7	526.6	492.0	420.1	313.3	173.0
323.15*	214.1	367.7	467.0	517.4	523.6	489.5	418.1	311.8	172.2
323.15**	218.4	372.6	470.6	519.1	523.7	488.8	417.6	312.0	173.0

* This work, extrapolated

** Lundberg[25] (Values at 298.15 K are integration constants)

Table 14 - continued

System n-Heptane-Toluene

	Mole Fraction n-Heptane								
	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9
T, K	Excess Entropy, J/mole K								
180.00*	0.981	1.630	2.010	2.168	2.147	1.975	1.670	1.243	0.690
190.00	0.887	1.470	1.808	1.946	1.923	1.765	1.490	1.107	0.614
200.00	0.807	1.336	1.640	1.762	1.737	1.591	1.342	0.995	0.552
210.00	0.739	1.222	1.498	1.607	1.582	1.447	1.219	0.903	0.500
220.00	0.681	1.124	1.377	1.475	1.451	1.326	1.116	0.826	0.457
230.00	0.630	1.039	1.272	1.363	1.339	1.223	1.028	0.761	0.421
240.00	0.584	0.965	1.181	1.265	1.243	1.135	0.954	0.705	0.390
250.00	0.544	0.898	1.100	1.178	1.158	1.058	0.889	0.657	0.363
260.00	0.507	0.839	1.027	1.102	1.084	0.990	0.832	0.615	0.339
270.00	0.474	0.784	0.962	1.033	1.017	0.929	0.781	0.577	0.318
280.00	0.443	0.735	0.903	0.971	0.957	0.875	0.736	0.544	0.300
290.00	0.415	0.690	0.850	0.915	0.904	0.828	0.697	0.515	0.284
298.15	0.395	0.657	0.810	0.874	0.865	0.793	0.668	0.494	0.272
300.00	0.390	0.650	0.802	0.866	0.856	0.786	0.662	0.490	0.270
310.00	0.367	0.614	0.760	0.822	0.815	0.750	0.632	0.468	0.258
320.00*	0.347	0.582	0.723	0.786	0.781	0.720	0.608	0.451	0.248

* Extrapolated

Table 14 - continued

System n-Heptane-Toluene

	Mole Fraction n-Heptane								
	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9
T, K	Excess Heat Capacity, J/mole K								
180.00*	-1.85	-3.15	-3.97	-4.39	-4.44	-4.17	-3.58	-2.70	-1.51
190.00	-1.64	-2.78	-3.49	-3.84	-3.87	-3.61	-3.10	-2.33	-1.31
200.00	-1.46	-2.47	-3.08	-3.37	-3.38	-3.15	-2.69	-2.02	-1.13
210.00	-1.32	-2.21	-2.75	-2.99	-2.98	-2.76	-2.36	-1.77	-0.99
220.00	-1.20	-2.00	-2.47	-2.67	-2.65	-2.45	-2.08	-1.55	-0.87
230.00	-1.10	-1.83	-2.24	-2.41	-2.38	-2.19	-1.85	-1.38	-0.77
240.00	-1.03	-1.69	-2.06	-2.20	-2.16	-1.98	-1.67	-1.24	-0.69
250.00	-0.96	-1.57	-1.91	-2.03	-1.98	-1.81	-1.52	-1.13	-0.63
260.00	-0.91	-1.48	-1.78	-1.89	-1.83	-1.66	-1.39	-1.03	-0.57
270.00	-0.86	-1.39	-1.67	-1.76	-1.70	-1.54	-1.28	-0.95	-0.53
280.00	-0.82	-1.32	-1.57	-1.64	-1.58	-1.42	-1.18	-0.87	-0.48
290.00	-0.77	-1.24	-1.47	-1.53	-1.46	-1.30	-1.08	-0.79	-0.44
298.15	-0.73	-1.17	-1.38	-1.42	-1.35	-1.20	-0.99	-0.72	-0.40
300.00	-0.72	-1.15	-1.35	-1.40	-1.32	-1.17	-0.96	-0.70	-0.39
310.00	-0.67	-1.05	-1.22	-1.24	-1.17	-1.02	-0.83	-0.60	-0.33
320.00*	-0.60	-0.93	-1.06	-1.06	-0.97	-0.84	-0.67	-0.48	-0.26
	Excess Volume, cm^3/mole								
293.15	0.051	0.091	0.121	0.139	0.146	0.142	0.125	0.096	0.055

* Extrapolated

Table 14 - continued

System n-Heptane-Toluene

	Mole Fraction n-Heptane (1)										
	0.0	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	1.0
T, K	Activity Coefficient γ_1										
180.00*	4.205	2.935	2.205	1.761	1.479	1.295	1.172	1.091	1.039	1.010	1.000
190.00	3.634	2.639	2.044	1.670	1.427	1.265	1.156	1.082	1.035	1.009	1.000
200.00	3.206	2.410	1.916	1.597	1.384	1.240	1.141	1.075	1.032	1.008	1.000
210.00	2.876	2.227	1.811	1.535	1.348	1.219	1.129	1.069	1.029	1.007	1.000
220.00	2.617	2.079	1.725	1.484	1.317	1.201	1.119	1.063	1.027	1.007	1.000
230.00	2.409	1.958	1.652	1.440	1.291	1.185	1.110	1.058	1.025	1.006	1.000
240.00	2.239	1.856	1.590	1.402	1.268	1.171	1.102	1.054	1.023	1.006	1.000
250.00	2.098	1.770	1.537	1.369	1.247	1.159	1.095	1.051	1.021	1.005	1.000
260.00	1.981	1.697	1.491	1.340	1.229	1.148	1.089	1.047	1.020	1.005	1.000
270.00	1.882	1.634	1.451	1.315	1.213	1.138	1.083	1.044	1.019	1.005	1.000
280.00	1.797	1.580	1.416	1.292	1.199	1.129	1.078	1.041	1.018	1.004	1.000
290.00	1.724	1.532	1.385	1.272	1.186	1.121	1.073	1.039	1.017	1.004	1.000
298.15	1.672	1.497	1.362	1.257	1.177	1.115	1.070	1.037	1.016	1.004	1.000
300.00	1.661	1.490	1.357	1.254	1.175	1.114	1.070	1.037	1.016	1.004	1.000
310.00	1.605	1.453	1.332	1.238	1.164	1.107	1.065	1.035	1.015	1.003	1.000
320.00*	1.557	1.420	1.310	1.223	1.154	1.101	1.061	1.033	1.014	1.003	1.000

* Extrapolated

Table 14 - continued

System n-Heptane-Toluene

	Mole Fraction n-Heptane (1)										
	0.0	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	1.0
T, K	Activity Coefficient γ_2										
180.00*	1.000	1.019	1.071	1.154	1.267	1.412	1.594	1.822	2.109	2.480	2.973
190.00	1.000	1.017	1.063	1.137	1.237	1.365	1.524	1.721	1.966	2.277	2.682
200.00	1.000	1.015	1.056	1.122	1.212	1.325	1.466	1.639	1.852	2.117	2.456
210.00	1.000	1.013	1.051	1.110	1.190	1.292	1.418	1.571	1.758	1.988	2.276
220.00	1.000	1.012	1.046	1.099	1.172	1.264	1.377	1.514	1.680	1.881	2.130
230.00	1.000	1.011	1.041	1.090	1.156	1.240	1.342	1.466	1.614	1.793	2.009
240.00	1.000	1.010	1.038	1.082	1.142	1.219	1.312	1.424	1.588	1.718	1.909
250.00	1.000	1.009	1.034	1.075	1.130	1.200	1.286	1.388	1.510	1.653	1.823
260.00	1.000	1.008	1.031	1.068	1.119	1.184	1.263	1.357	1.468	1.598	1.750
270.00	1.000	1.007	1.029	1.063	1.110	1.170	1.242	1.329	1.431	1.550	1.687
280.00	1.000	1.007	1.026	1.058	1.101	1.157	1.224	1.305	1.399	1.507	1.631
290.00	1.000	1.006	1.024	1.054	1.094	1.145	1.208	1.283	1.370	1.470	1.583
298.15	1.000	1.006	1.023	1.050	1.088	1.137	1.197	1.267	1.349	1.442	1.547
300.00	1.000	1.006	1.022	1.050	1.087	1.135	1.194	1.264	1.344	1.436	1.540
310.00	1.000	1.005	1.021	1.046	1.081	1.126	1.181	1.246	1.321	1.406	1.502
320.00*	1.000	1.005	1.019	1.043	1.076	1.118	1.169	1.230	1.300	1.379	1.467

* Extrapolated

Table 14 - continued

System Methylcyclohexane-Toluene

	Mole Fraction Methylcyclohexane								
	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9
T, K	Excess Gibbs Free Energy, J/mole								
160.00*	167.3	291.1	375.4	423.4	437.1	417.8	365.7	280.0	159.0
170.00	159.0	277.1	357.8	403.7	416.7	397.9	347.7	265.7	150.4
180.00	151.2	263.9	341.1	385.0	397.4	379.2	330.8	252.2	142.4
190.00	143.9	251.5	325.4	367.5	379.1	361.5	314.9	239.6	134.9
200.00	137.0	239.9	310.7	351.0	362.1	344.9	300.1	227.8	128.0
210.00	130.7	229.1	296.9	335.5	346.1	329.4	286.2	216.9	121.5
220.00	124.8	219.0	284.1	321.1	331.1	315.0	273.4	206.8	115.6
230.00	119.3	209.6	272.1	307.7	317.2	301.5	261.4	197.4	110.1
240.00	114.2	200.9	260.9	295.1	304.2	289.0	250.3	188.7	105.0
250.00	109.5	192.7	250.5	283.4	292.0	277.3	239.9	180.7	100.4
260.00	105.1	185.2	240.7	272.3	280.7	266.4	230.3	173.2	96.1
270.00	101.0	178.1	231.6	262.0	270.0	256.1	221.3	166.3	92.2
280.00	97.2	171.4	223.0	252.3	259.9	246.5	212.9	159.9	88.6
283.15	96.1	169.4	220.4	249.3	256.9	243.6	210.4	158.0	87.5
290.00	93.7	165.2	214.9	243.1	250.4	237.5	205.0	154.0	85.2
298.15	91.0	160.4	208.6	236.0	243.1	230.5	199.0	149.4	82.7
300.00	90.4	159.4	207.2	234.4	241.4	228.9	197.7	148.4	82.2
310.00	87.3	153.9	200.0	226.2	232.9	220.9	190.7	143.3	79.4
320.00	84.5	148.7	193.2	218.4	224.9	213.3	184.2	138.5	76.8
330.00	81.8	143.8	186.7	211.0	217.2	206.1	178.1	134.0	74.4
333.15**	81.0	142.4	184.8	208.7	214.9	203.9	176.3	132.7	73.7
353.15**	75.9	133.2	172.6	194.7	200.2	189.7	163.8	123.1	68.3
363.15**	72.0	126.9	165.1	187.0	193.0	183.6	159.2	120.2	67.0
373.15**	69.1	121.4	157.6	178.0	183.3	174.0	150.4	113.2	62.9
373.15*	72.7	126.7	163.5	184.1	189.5	180.3	156.8	119.1	67.0

* This work, extrapolated

** Schneider[40] (Values at 333.15 K are integration constants)

Table 14 - continued

System Methycyclohexane-Toluene

	Mole Fraction Methylcylochexane								
	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9
T, K	Excess Enthalpy, J/mole								
160.00*	303.7	520.5	664.5	746.2	771.7	743.6	659.9	515.2	299.8
170.00	296.0	508.1	649.5	729.7	754.7	726.6	644.0	501.8	291.3
180.00	287.5	494.4	632.6	711.1	735.3	707.4	626.1	486.9	282.0
190.00	278.5	479.6	614.4	691.0	714.5	686.8	607.0	471.1	272.1
200.00	269.1	464.3	595.5	670.0	692.6	665.2	587.0	454.6	261.9
210.00	259.6	448.7	576.2	648.7	670.5	643.3	566.8	437.9	251.5
220.00	250.1	433.2	557.0	627.4	648.4	621.5	546.6	421.3	241.2
230.00	240.8	417.9	538.2	606.6	626.7	600.1	526.8	404.9	231.1
240.00	231.8	403.2	520.0	586.6	605.9	579.5	507.7	389.1	221.2
250.00	223.1	389.1	502.7	567.5	586.0	559.9	489.4	373.9	211.7
260.00	214.8	375.7	486.3	549.4	567.3	541.3	472.0	359.4	202.6
270.00	207.0	363.1	470.9	532.5	549.7	523.8	455.7	345.7	193.9
280.00	199.6	351.2	456.5	516.8	533.4	507.5	440.3	332.7	185.7
283.15**	197.3	347.6	452.1	512.0	528.4	502.6	435.6	328.8	183.2
290.00	192.5	340.0	443.0	502.0	518.0	492.2	425.8	320.4	177.8
298.15	187.0	331.3	432.5	490.6	506.2	480.3	414.5	310.8	171.6
298.15**	192.8	339.9	442.4	501.2	517.6	492.6	427.2	332.6	179.8
300.00	185.8	329.4	430.2	488.1	503.6	477.7	412.0	308.6	170.2
310.00	179.3	319.1	417.9	474.7	489.7	463.8	398.7	297.3	162.9
320.00*	172.8	309.0	405.8	461.6	476.1	450.1	385.7	286.0	155.6

* This work, extrapolated

**Sosnkowska-Kehiahian[44] (Values at 283.15 K are integration constants.)

Table 14 - continued

System Methylcyclohexane-Toluene

	Mole Fraction Methylcyclohexane								
	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9
T, K	Excess Entropy, J/mole K								
160.00*	0.852	1.433	1.807	2.018	2.092	2.036	1.839	1.470	0.880
170.00	0.806	1.359	1.716	1.918	1.988	1.933	1.743	1.389	0.829
180.00	0.757	1.280	1.620	1.812	1.878	1.824	1.640	1.304	0.775
190.00	0.709	1.200	1.521	1.703	1.765	1.712	1.537	1.218	0.722
200.00	0.660	1.121	1.424	1.595	1.653	1.602	1.435	1.134	0.670
210.00	0.614	1.046	1.330	1.491	1.545	1.495	1.336	1.053	0.619
220.00	0.570	0.973	1.240	1.392	1.442	1.393	1.242	0.975	0.571
230.00	0.528	0.906	1.157	1.300	1.346	1.298	1.154	0.902	0.526
240.00	0.490	0.843	1.079	1.214	1.257	1.210	1.073	0.835	0.484
250.00	0.455	0.785	1.009	1.136	1.176	1.130	0.998	0.773	0.445
260.00	0.422	0.733	0.944	1.066	1.102	1.057	0.930	0.716	0.410
270.00	0.393	0.685	0.886	1.002	1.036	0.991	0.868	0.664	0.377
280.00	0.366	0.642	0.834	0.945	0.977	0.932	0.812	0.617	0.347
283.15	0.358	0.629	0.819	0.928	0.959	0.915	0.796	0.603	0.338
290.00	0.341	0.603	0.786	0.893	0.923	0.878	0.761	0.574	0.319
298.15	0.322	0.573	0.751	0.854	0.883	0.838	0.723	0.541	0.298
300.00	0.318	0.567	0.743	0.845	0.874	0.829	0.715	0.534	0.294
310.00	0.297	0.533	0.703	0.802	0.828	0.784	0.671	0.497	0.269
320.00*	0.276	0.501	0.664	0.760	0.785	0.740	0.629	0.461	0.246

* Extrapolated

Table 14 - continued

System Methylcyclohexane-Toluene

	Mole Fraction Methylcyclohexane								
	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9
T, K	Excess Heat Capacity, J/mole K								
160.00*	-0.72	-1.14	-1.38	-1.51	-1.57	-1.57	-1.48	-1.25	-0.80
170.00	-0.81	-1.31	-1.60	-1.76	-1.83	-1.82	-1.70	-1.42	-0.90
180.00	-0.88	-1.43	-1.76	-1.95	-2.02	-2.00	-1.86	-1.54	-0.96
190.00	-0.92	-1.51	-1.87	-2.06	-2.14	-2.12	-1.96	-1.62	-1.01
200.00	-0.95	-1.55	-1.92	-2.12	-2.21	-2.18	-2.02	-1.66	-1.03
210.00	-0.95	-1.56	-1.93	-2.14	-2.22	-2.19	-2.03	-1.67	-1.04
220.00	-0.94	-1.54	-1.91	-2.11	-2.19	-2.16	-2.00	-1.65	-1.02
230.00	-0.92	-1.50	-1.85	-2.05	-2.13	-2.10	-1.95	-1.61	-1.00
240.00	-0.89	-1.44	-1.78	-1.96	-2.04	-2.02	-1.87	-1.55	-0.97
250.00	-0.85	-1.37	-1.69	-1.86	-1.93	-1.91	-1.78	-1.49	-0.93
260.00	-0.81	-1.30	-1.59	-1.75	-1.81	-1.80	-1.69	-1.41	-0.89
270.00	-0.76	-1.22	-1.49	-1.63	-1.70	-1.69	-1.59	-1.33	-0.85
280.00	-0.72	-1.15	-1.39	-1.52	-1.58	-1.58	-1.49	-1.26	-0.81
283.15	-0.71	-1.13	-1.37	-1.49	-1.55	-1.55	-1.46	-1.24	-0.79
290.00	-0.69	-1.09	-1.31	-1.43	-1.49	-1.49	-1.41	-1.20	-0.77
298.15	-0.67	-1.05	-1.26	-1.37	-1.42	-1.43	-1.36	-1.16	-0.75
300.00	-0.66	-1.04	-1.25	-1.36	-1.41	-1.42	-1.35	-1.15	-0.74
310.00	-0.65	-1.01	-1.21	-1.32	-1.37	-1.37	-1.31	-1.13	-0.73
320.00*	-0.64	-1.01	-1.21	-1.32	-1.37	-1.37	-1.31	-1.12	-0.73
	Excess Volume, cm^3/mole								
293.15	0.127	0.231	0.311	0.364	0.388	0.382	0.342	0.266	0.153

* Extrapolated

Table 14 - continued

System Methylcyclohexane-Toluene

	Mole Fraction Methylcyclohexane										
	0.0	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	1.0
T, K	Activity Coefficient γ_1										
160.00	4.193	3.020	2.319	1.874	1.578	1.374	1.230	1.127	1.057	1.015	1.000
170.00	3.595	2.693	2.129	1.759	1.506	1.329	1.202	1.112	1.050	1.013	1.000
180.00	3.147	2.439	1.977	1.665	1.446	1.291	1.179	1.099	1.044	1.011	1.000
190.00	2.805	2.237	1.853	1.587	1.396	1.259	1.159	1.087	1.039	1.010	1.000
200.00	2.538	2.075	1.752	1.521	1.354	1.232	1.142	1.078	1.034	1.009	1.000
210.00	2.326	1.942	1.667	1.466	1.318	1.208	1.127	1.069	1.030	1.008	1.000
220.00	2.156	1.833	1.596	1.419	1.287	1.188	1.115	1.062	1.027	1.007	1.000
230.00	2.016	1.742	1.535	1.379	1.260	1.171	1.104	1.056	1.024	1.006	1.000
240.00	1.901	1.665	1.483	1.344	1.237	1.155	1.095	1.051	1.022	1.005	1.000
250.00	1.805	1.599	1.439	1.314	1.216	1.142	1.087	1.047	1.020	1.005	1.000
260.00	1.724	1.543	1.400	1.287	1.199	1.130	1.079	1.043	1.018	1.004	1.000
270.00	1.655	1.494	1.366	1.263	1.183	1.120	1.073	1.039	1.017	1.004	1.000
280.00	1.596	1.452	1.336	1.242	1.168	1.111	1.067	1.036	1.015	1.004	1.000
283.15	1.579	1.440	1.327	1.236	1.164	1.108	1.066	1.035	1.015	1.004	1.000
290.00	1.545	1.415	1.309	1.224	1.156	1.103	1.062	1.033	1.014	1.003	1.000
298.15	1.508	1.388	1.290	1.210	1.146	1.097	1.059	1.032	1.013	1.003	1.000
300.00	1.500	1.382	1.285	1.207	1.144	1.095	1.058	1.031	1.013	1.003	1.000
310.00	1.461	1.353	1.264	1.192	1.134	1.089	1.054	1.029	1.012	1.003	1.000
320.00	1.427	1.327	1.245	1.178	1.125	1.083	1.051	1.027	1.012	1.003	1.000
330.00	1.398	1.304	1.228	1.166	1.116	1.077	1.048	1.026	1.011	1.003	1.000
333.15**	1.389	1.297	1.223	1.162	1.114	1.076	1.047	1.025	1.011	1.003	1.000
353.15**	1.337	1.258	1.194	1.141	1.099	1.066	1.040	1.022	1.009	1.002	1.000
363.15**	1.306	1.237	1.180	1.132	1.094	1.063	1.039	1.021	1.009	1.002	1.000
373.15**	1.284	1.219	1.165	1.121	1.086	1.057	1.035	1.019	1.008	1.002	1.000
373.15*	1.305	1.229	1.170	1.124	1.088	1.060	1.038	1.021	1.010	1.002	1.000

* This work, extrapolated
** Schneider[40]

Table 14 - continued

System Methylcyclohexane-Toluene

	Mole Fraction Methylcyclohexane (1)										
	0.0	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	1.0
T, K	Activity Coefficient γ_2										
160.00*	1.000	1.017	1.065	1.143	1.254	1.404	1.608	1.890	2.293	2.895	3.843
170.00	1.000	1.015	1.058	1.127	1.225	1.357	1.534	1.773	2.106	2.585	3.303
180.00	1.000	1.013	1.051	1.113	1.200	1.318	1.472	1.678	1.956	2.344	2.900
190.00	1.000	1.012	1.046	1.101	1.180	1.284	1.420	1.599	1.835	2.153	2.592
200.00	1.000	1.011	1.041	1.091	1.162	1.255	1.376	1.533	1.735	1.999	2.353
210.00	1.000	1.009	1.037	1.082	1.146	1.230	1.339	1.477	1.651	1.875	2.163
220.00	1.000	1.009	1.033	1.075	1.133	1.209	1.306	1.429	1.581	1.772	2.010
230.00	1.000	1.008	1.030	1.068	1.121	1.190	1.278	1.388	1.522	1.686	1.886
240.00	1.000	1.007	1.028	1.062	1.110	1.174	1.254	1.352	1.471	1.614	1.784
250.00	1.000	1.006	1.025	1.057	1.101	1.160	1.233	1.321	1.428	1.553	1.699
260.00	1.000	1.006	1.023	1.052	1.093	1.147	1.214	1.294	1.390	1.500	1.627
270.00	1.000	1.005	1.021	1.048	1.086	1.136	1.197	1.270	1.356	1.455	1.567
280.00	1.000	1.005	1.020	1.045	1.080	1.125	1.182	1.249	1.327	1.416	1.516
283.15	1.000	1.005	1.019	1.044	1.078	1.122	1.177	1.243	1.318	1.405	1.501
290.00	1.000	1.005	1.018	1.042	1.074	1.116	1.168	1.230	1.301	1.382	1.471
298.15	1.000	1.004	1.017	1.039	1.070	1.109	1.158	1.216	1.282	1.357	1.440
300.00	1.000	1.004	1.017	1.039	1.069	1.108	1.156	1.212	1.278	1.352	1.433
310.00	1.000	1.004	1.016	1.036	1.064	1.100	1.145	1.197	1.257	1.325	1.400
320.00	1.000	1.004	1.015	1.034	1.060	1.094	1.135	1.183	1.239	1.302	1.372
330.00	1.000	1.004	1.014	1.032	1.056	1.087	1.125	1.170	1.222	1.281	1.347
333.15**	1.000	1.004	1.014	1.031	1.055	1.086	1.123	1.166	1.217	1.275	1.339
353.15**	1.000	1.003	1.013	1.028	1.049	1.075	1.108	1.145	1.188	1.237	1.290
363.15**	1.000	1.003	1.011	1.025	1.044	1.069	1.099	1.135	1.176	1.224	1.276
373.15**	1.000	1.003	1.011	1.024	1.042	1.064	1.092	1.124	1.161	1.203	1.250
373.15*	1.000	1.003	1.012	1.025	1.044	1.066	1.094	1.127	1.167	1.214	1.272

* This work, extrapolated
** Schneider[40]

Table 14 - continued

System n-Heptane-Methylcyclohexane

Mixture Composition 0.48910 Mole Fraction n-Heptane

T	$\tilde{G}^E$	$\tilde{H}^E$	$\tilde{S}^E$	$\tilde{C}_p^E$	$\tilde{V}^E$
K	J/mole	J/mole	J/mole K	J/mole K	cm^3/mole
180.00	63.9*	324.7*	1.449*	-5.70*	
190.00	50.9	272.5	1.167	-4.76	
200.00	40.4	229.0	0.943	-3.97	
210.00	31.9	192.7	0.766	-3.32	
220.00	24.9	162.3	0.624	-2.78	
230.00	19.3	136.7	0.510	-2.35	
240.00	14.7	114.9	0.418	-2.01	
250.00	10.9	96.2	0.341	-1.74	
260.00	7.8	80.0	0.278	-1.52	
270.00	5.3	65.7	0.224	-1.34	
280.00	3.3	53.1	0.178	-1.18	
290.00	1.7	42.0	0.139	-1.03	
293.15	1.3	39.1	0.129	-0.97	-0.011
298.15	0.7	34.2**	0.112	-0.89	
300.00	0.5	32.6	0.107	-0.86	
304.65	0.0***	28.8	0.094	-0.77	
310.00	-0.4	25.0	0.082	-0.66	
320.00	-1.2*	19.5*	0.064*	-0.42*	
320.64	0.0***				
323.15	-1.4*	18.3*	0.061*	-0.34*	
323.15		18.6**			
353.10	-3.2*				
353.10	0.0***				

* Extrapolated

** Lundberg[25] (Value at 298.15 K is integration constant)

*** Brandt and Roeck[9] (Value at 304.65 K is integration constant)

APPENDIX F

CONFIGURATIONAL ENERGY AND VOLUME OF LIQUID TOLUENE

In classical statistical mechanics, the configurational energy of a liquid is equal to the energy difference between the liquid and the ideal gas at the same temperature, provided that the internal energies of the molecules are not affected by their environment.* This energy difference is composed of two parts: the energy of vaporization at constant temperature and pressure, and the energy difference between the real gas and the ideal gas at the same temperature. At low pressures, the latter part is negligible compared to the energy of vaporization. The expression for the configurational energy, $\tilde{U}_o$, then reduces to

$$\tilde{U}_o = \tilde{U}_{gas} - \tilde{U}_{liquid} = - \tilde{U}_v = - \tilde{H}_v + P (\tilde{V}_{gas} - \tilde{V}_{liquid}) \qquad (94)$$

If the volume of the liquid is neglected compared to that of the vapor, and the ideal gas law is assumed to be valid, Equation (94) becomes

$$\tilde{U}_o = - \tilde{H}_v + R T \qquad (95)$$

If the heat of vaporization is known at one temperature, T_o, it can be computed for any other temperature, T, provided the heat capacities of the liquid and the gas are known over the range between T_o and T:

---

* A more detailed discussion of configurational properties is given by Rowlinson (Reference 35, Chapter II).

$$\tilde{H}_v(T) = \tilde{H}_v(T_o) + \int_{T_o}^{T} (\tilde{C}_{p\ gas} - \tilde{C}_{p\ liquid})\ dT \qquad (96)$$

This formula is only valid if the pressure effect on the thermodynamic properties is negligible. The configurational energy is then given by the expression

$$\tilde{U}_o(T) = -\tilde{H}_v(T_o) - \int_{T_o}^{T} (\tilde{C}_{p\ gas} - \tilde{C}_{p\ liquid})\ dT + R\ T \qquad (97)$$

At low pressures, the ideal gas heat capacity may be substituted for $\tilde{C}_{p\ gas}$. Ideal gas functions of toluene have been computed by Scott et al.[41] assuming free rotation of the methyl group. Since the authors do not list their results for a sufficient number of temperatures to permit interpolation, the heat capacity was computed at ten degree intervals between 160 and 370 K using the frequencies given by Scott et al. and fitted by a polynomial (units: J, mole, K):

$$\tilde{C}_{p\ gas} = 40.886080 - 8.2172468\times10^{-2}\ T + 1.4454343\times10^{-3}\ T^2 - 1.5605697\times10^{-6}\ T^3 \qquad (98)$$

The heat capacity of the liquid was taken from this work; the polynomial used is given in Table 9, Appendix C. The heat of vaporization at 298.15 K was taken from the API Tables[2]:

$$\tilde{H}_v\ (298.15\ K) = 37991\ J/mole \qquad (99)$$

By inserting these results into Equation (97), the configurational energy of toluene is found to be

$$\tilde{U}_o = -63693.102 + 154.86636\ T - 0.32404623\ T^2 + 5.053086\ 10^{-4}\ T^3 - 3.2640018\ 10^{-7}\ T^4 \quad (100)$$

The density of liquid toluene is listed in the API Tables[2] at ten degree intervals from 183.15 to 383.15 K. From these values, the molar volumes were computed and fitted by a polynomial (units: cm^3, mole, K):

$$\tilde{V}_o = 80.430085 + 7.4025442\text{x}10^{-2}\ T + 1.1405825\text{x}10^{-5}\ T^2 + 1.2595624\text{x}10^{-7}\ T^3 \quad (101)$$

APPENDIX G

THEORETICAL CORRELATIONS OF THE DERIVED EXCESS THERMODYNAMIC PROPERTIES

Table 15. Comparison of Various Fits of the Derived Excess Thermodynamic Properties for Equimolar Mixtures

System n-Heptane-Toluene

Method No.	Quantities Fitted	e_{12}	d_{12} K	s_{12}	V^E (293.15 K) cm^3/mole
expt.					0.1464
	Conformal Solution Theory [24]				
1	G^E (182-312 K)	-0.03636			0.3016
2	G^E (182-312 K) V^E (293.15 K)	-0.03606		-0.001916	(0.1464)
	Theory of Rowlinson and Sutton [37]				
3	G^E (182-312 K)		-4.343		0.6394
4	G^E (182-312 K) V^E (293.15 K)		-4.239	-0.006108	(0.1464)
5	G^E (182-312 K)	-0.02136	-1.820		0.4451
6	G^E (182-312 K) V^E (293.15 K)	-0.01994	-1.918	-0.003834	(0.1464)
7	G^E (293.15 K) H^E (293.15 K)	-0.02194	-1.737		0.4451
8	G^E (293.15 K) H^E (293.15 K) V^E (293.15 K)	-0.02007	-1.904	-0.003770	(0.1464)
	Theory of Flory [15]				
9	H^E (182-312 K)				0.2639
10	H^E (298.15 K)				0.2641

Table 15 - Continued

System n-Heptane-Toluene

Method	Temperature, K					
	182	208	234	260	286	312
	Excess Gibbs Free Energy, J/mole					
expt.	447.5	399.7	362.2	331.4	305.4	282.9
1	395.9	377.9	360.9	344.9	329.7	315.1
2	394.8	377.1	360.7	345.1	330.4	316.2
3	510.6	424.9	359.4	307.9	266.4	232.2
4	505.3	422.6	359.7	310.4	270.9	238.6
5	446.5	399.9	362.5	331.5	305.2	282.3
6	447.0	399.9	362.3	331.4	305.3	282.9
7	443.1	397.9	361.5	331.3	305.5	283.0
8	446.7	399.7	362.3	331.5	305.5	283.1
9	722.6	624.6	551.3	493.0	443.9	402.7
10	469.7	460.1	450.1	439.7	429.0	417.7
	Excess Enthalpy, J/mole K					
expt.	829.4	734.8	666.2	613.1	569.7	535.0
1	527.1	517.6	508.8	500.7	493.4	487.0
2	522.6	513.2	504.4	496.4	489.3	482.8
3	1202.4	1019.3	878.7	767.9	678.5	605.0
4	1173.5	994.9	857.7	749.4	662.2	590.5
5	813.4	731.1	667.0	615.8	574.1	539.5
6	820.1	734.0	667.1	613.7	570.3	534.3
7	798.9	720.0	658.4	609.2	569.1	535.8
8	818.1	732.6	666.1	613.0	569.8	534.0
9	(829.4)	(734.8)	(666.2)	(613.1)	(569.7)	(535.0)
10	536.4	538.6	541.6	545.2	549.9	555.7

Table 15 - continued

System n-Heptane-Toluene

Method	Temperature, K					
	182	208	234	260	286	312
	Excess Entropy, J/mole K					
expt.	2.099	1.611	1.299	1.084	0.924	0.808
1	0.721	0.672	0.632	0.599	0.572	0.551
2	0.702	0.654	0.614	0.582	0.556	0.534
3	3.801	2.858	2.219	1.769	1.441	1.195
4	3.672	2.751	2.128	1.689	1.368	1.128
5	2.016	1.592	1.301	1.093	0.940	0.824
6	2.050	1.607	1.303	1.086	0.926	0.806
7	1.955	1.548	1.269	1.069	0.922	0.810
8	2.041	1.600	1.298	1.083	0.924	0.804
9	0.587	0.530	0.491	0.462	0.440	0.424
10	0.366	0.378	0.391	0.406	0.423	0.442
	Excess Volume, cm^3/mole					
1	0.150	0.180	0.213	0.249	0.290	0.334
2	0.012	0.038	0.067	0.100	0.136	0.176
3	0.764	0.715	0.681	0.658	0.642	0.634
4	0.310	0.252	0.207	0.172	0.144	0.121
5	0.408	0.405	0.410	0.422	0.439	0.462
6	0.146	0.134	0.130	0.132	0.139	0.151
7	0.396	0.395	0.401	0.414	0.432	0.455
8	0.149	0.137	0.133	0.136	0.143	0.156
9	0.228	0.234	0.243	0.252	0.260	0.268
10	0.115	0.141	0.171	0.204	0.244	0.290

Table 15 - continued

System Methylcyclohexane-Toluene

Method No.	Quantities Fitted	e_{12}	d_{12} K	s_{12}	V^E (293.15 K) cm^3/mole
expt.					0.3885
	Conformal Solution Theory [24]				
1	G^E (162-312 K)	-0.03216			0.2667
2	G^E (162-312 K) V^E (293.15 K)	-0.03236		-0.001506	(0.3885)
	Theory of Rowlinson and Sutton [37]				
3	G^E (162-312 K)		-3.600		0.5300
4	G^E (162-312 K) V^E (293.15 K)		-3.576	-0.001828	(0.3885)
5	G^E (162-312 K)	-0.01478	-1.978		0.4139
6	G^E (162-312 K) V^E (293.15 K)	-0.01466	-1.986	-0.000373	(0.3885)
7	G^E (293.15 K) H^E (293.15 K)	-0.01283	-2.248		0.4375
8	G^E (293.15 K) H^E (293.15 K) V^E (293.15 K)	-0.01251	-2.276	-0.000633	(0.3885)
	Theory of Flory [15]				
9	H^E (162-312 K)				0.3557
10	H^E (298.15 K)				0.3491

Table 15 - continued

System Methylcyclohexane-Toluene

Method	Temperature, K					
	162	192	222	252	282	312
	Excess Gibbs Free Energy, J/mole					
expt.	432.9	375.6	328.3	289.7	258.0	231.3
1	363.3	343.9	326.0	309.3	293.6	278.7
2	364.1	344.3	326.0	308.9	292.9	277.5
3	494.6	393.5	321.3	267.3	225.6	192.5
4	493.1	393.1	321.7	268.4	227.4	194.8
5	438.8	374.3	326.4	289.1	259.0	233.9
6	438.8	374.3	326.4	289.1	259.0	234.0
7	453.8	382.9	330.7	290.4	258.1	231.4
8	454.7	383.4	330.9	290.4	258.1	231.4
9	680.9	611.3	536.9	468.5	409.9	359.5
10	432.9	422.5	411.7	400.4	388.6	376.2
	Excess Enthalpy, J/mole					
expt.	768.6	710.1	644.0	582.2	530.2	487.0
1	472.8	462.8	453.4	444.9	437.3	430.6
2	475.8	465.8	456.3	447.8	440.1	433.4
3	1148.0	933.2	778.6	662.6	572.8	501.5
4	1140.4	927.0	773.4	658.2	569.0	498.2
5	848.2	725.5	636.3	568.6	515.8	473.5
6	848.8	725.8	636.2	568.3	515.4	473.0
7	905.6	767.5	667.1	591.3	532.2	485.0
8	909.9	770.2	668.8	592.1	532.4	484.7
9	(768.6)	(710.1)	(644.0)	(582.2)	(530.2)	(487.0)
10	487.9	490.2	493.2	497.2	502.6	509.7

Table 15 - continued

System Methylcyclohexane-Toluene

Method	Temperature, K					
	162	192	222	252	282	312
	Excess Entropy, J/mole K					
expt.	2.072	1.742	1.422	1.161	0.965	0.819
1	0.676	0.620	0.574	0.538	0.510	0.487
2	0.690	0.633	0.587	0.551	0.522	0.500
3	4.034	2.811	2.060	1.569	1.231	0.990
4	3.996	2.781	2.035	1.547	1.212	0.972
5	2.527	1.829	1.396	1.109	0.911	0.768
6	2.531	1.831	1.396	1.108	0.909	0.766
7	2.789	2.003	1.516	1.194	0.972	0.813
8	2.810	2.015	1.522	1.197	0.973	0.812
9	0.540	0.515	0.482	0.451	0.427	0.408
10	0.340	0.352	0.367	0.384	0.404	0.428
	Excess Volume, cm^3/mole					
1	0.114	0.143	0.174	0.210	0.251	0.296
2	0.220	0.252	0.287	0.327	0.372	0.420
3	0.676	0.616	0.576	0.550	0.534	0.525
4	0.543	0.480	0.437	0.407	0.387	0.373
5	0.424	0.404	0.397	0.399	0.409	0.425
6	0.399	0.378	0.370	0.371	0.379	0.394
7	0.468	0.442	0.430	0.428	0.434	0.446
8	0.427	0.399	0.385	0.382	0.385	0.396
9	0.209	0.246	0.278	0.308	0.342	0.381
10	0.125	0.161	0.205	0.257	0.321	0.402

Table 15 - Continued

System Methylcyclohexane-Toluene

Method	Temperature, K			
	333.15	353.15	363.15	373.15
	Excess Gibbs Free Energy, J/mole			
expt.*	214.9	200.2	193.0	183.3
5	215.2	201.3	194.9	188.8
6	215.2	201.4	195.0	188.9

* Schneider[40]

Table 16. Contributions of Various Interaction Parameters to the Predicted Excess Thermodynamic Properties Using the Theory of Rowlinson and Sutton.[37] (Based on Method 6, see Table 15)

System n-Heptane-Toluene

Parameter	Temperature, K					
	182	208	234	260	286	312
	Excess Gibbs Free Energy, J/mole					
e_{12}	217.1	207.2	197.9	189.2	180.8	172.8
d_{12}	225.5	187.7	158.7	136.0	117.6	102.6
s_{12}	4.4	5.0	5.6	6.2	6.8	7.5
total	447.0	399.9	362.3	331.4	305.3	282.9
	Excess Enthalpy, J/mole					
e_{12}	289.1	283.9	279.0	274.6	270.6	267.0
d_{12}	531.0	450.2	388.1	339.1	299.6	267.2
total	820.1	734.0	667.1	613.7	570.3	534.3
	Excess Entropy, J/mole K					
e_{12}	0.395	0.368	0.346	0.329	0.314	0.302
d_{12}	1.679	1.262	0.980	0.781	0.636	0.528
s_{12}	-0.024	-0.024	-0.024	-0.024	-0.024	-0.024
total	2.050	1.607	1.303	1.086	0.926	0.806
	Excess Volume, cm^3/mole					
e_{12}	0.082	0.099	0.117	0.137	0.159	0.183
d_{12}	0.337	0.316	0.301	0.291	0.284	0.280
s_{12}	-0.273	-0.280	-0.287	-0.295	-0.303	-0.312
total	0.146	0.134	0.130	0.132	0.139	0.151

Table 16 - continued

System Methylcyclohexane-Toluene

Parameter	Temperature, K					
	162	192	222	252	282	312
	Excess Gibbs Free Energy, J/mole					
e_{12}	165.6	156.8	148.6	141.0	133.9	127.1
d_{12}	272.8	217.1	177.2	147.5	124.5	106.2
s_{12}	0.4	0.4	0.5	0.6	0.7	0.7
total	438.8	374.3	326.4	289.1	259.0	234.0
	Excess Enthalpy, J/mole					
e_{12}	215.6	211.0	206.7	202.8	199.4	196.3
d_{12}	633.3	514.8	429.5	365.5	316.0	276.6
total	848.8	725.8	636.2	568.3	515.4	473.0
	Excess Entropy, J/mole K					
e_{12}	0.308	0.283	0.262	0.245	0.232	0.222
d_{12}	2.225	1.551	1.136	0.865	0.679	0.546
s_{12}	-0.002	-0.002	-0.002	-0.002	-0.002	-0.002
total	2.531	1.831	1.396	1.108	0.909	0.766
	Excess Volume, cm^3/mole					
e_{12}	0.052	0.065	0.080	0.096	0.114	0.135
d_{12}	0.373	0.340	0.318	0.304	0.295	0.290
s_{12}	-0.026	-0.027	-0.028	-0.029	-0.029	-0.030
total	0.399	0.378	0.370	0.371	0.379	0.394

Table 17. Interaction Parameter X_{12} Derived from the Theory of Flory[15]

x_1	X_{12} (T = 298.15 K) J/cm^3	
	n-Heptane (1) -Toluene	Methylcyclohexane(1) -Toluene
0.1	22.20	20.04
0.2	21.75	20.17
0.3	21.34	20.28
0.4	20.99	20.36
0.5	20.69	20.39
0.6	20.45	20.38
0.7	20.29	20.33
0.8	20.19	20.22
0.9	20.17	20.07

T K	X_{12} (x_1 = 0.5) J/cm^3	
	n-Heptane(1) -Toluene	Methylcyclohexane(1) -Toluene
160.00		32.25
170.00		31.50
180.00	32.32	30.64
190.00	30.67	29.72
200.00	29.23	28.76
210.00	27.96	27.79
220.00	26.82	26.81
230.00	25.81	25.85
240.00	24.88	24.93
250.00	24.04	24.04
260.00	23.25	23.20
270.00	22.51	22.40
280.00	21.82	21.66
290.00	21.18	20.95
298.15	20.69	20.39
300.00	20.58	20.26
310.00	20.03	19.62
320.00	19.55	18.96

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